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PHOTOCHEMISTRY

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BY

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WITH A PREFACE BY

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WITH 9 DIAGRAMS



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PREFACE

THE study and the understanding of the chemical action of light, more so than of any other branch of chemical kinetics, owe much to contemporary physics. And to their appreciation of this fact, chemists working in the field add a lively anticipation of further favours to come.

The inclusion of a volume on Photochemistry in this series of monographs is not, however, merely an act of homage. Still less is it an intrusion. For the subject is one abounding in interest to the physicist, as will readily be gathered by anyone who reads the pages which follow.

The author has treated his theme in broad outline, emphasizing its physical aspects and avoiding any attempt to compress a mass of chemical facts within the limits assigned him. His illustrative examples are few, but adequate and to the point.

The present writer is convinced that this form of approach to photochemistry, an obvious one for the physicist, is also the best for the chemist who has not hitherto interested himself in the subject. The chemical detail can come later. He therefore recommends the present volume with confidence to students and research workers in both the sciences.

A. J. ALLMAND

KING'S COLLEGE, LONDON

September, 1930

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PHOTOCHEMISTRY

CHAPTER I

INTRODUCTORY

IT is only in the present century that photochemistry, or the study of the chemical changes induced by light, has developed its individuality, and it must now be considered as one of the most valuable instruments for the elucidation of the true mechanisms of chemical processes. Prior to the present rapid advance in the realm of atomic physics the theoretical difficulties barred any real progress in our subject, but as soon as the chemist realized the value of the new physical theories, he began to apply them with conspicuous success to his own problems.

As witnessed by the solar deities of mythology, the importance of light to living things must have been realized early in man's history and practical use has been made of sunlight for bleaching purposes for several thousand years. We have, however, to turn to the beginning of the eighteenth century to find further recognition of a connexion between light and chemical change, the observation being then made of the darkening on exposure to light of some silver salts which was later to lead to the discovery of ultraviolet radiation. The second half of this century and the beginning of the nineteenth saw the opening of the attack on numerous photoreactions which resulted in the formulation of the important generalization, known as the Grotthus-Draper law, that only light which is absorbed by the reacting system can produce chemical change. It was also demonstrated that for the reactions then known

the amount of chemical change was proportional to the product of the light intensity and the duration of the illumination, or as more recent work has shown (with certain important exceptions) proportional to the total quantity of light energy absorbed.

In this connexion the laws of light absorption become of importance. These laws were discovered by Beer and Lambert and can be combined in the form :

$$\log_e \frac{I_0}{I} = \epsilon cd \quad . \quad . \quad . \quad (1a)$$

or as is more usual, using decadic logarithms

$$\log_{10} \frac{I_0}{I} = acd \quad . \quad . \quad . \quad (1b)$$

in which I_0 and I are respectively the incident and transmitted intensities of a parallel beam of light which passes normally through a layer of the absorbing substance of thickness d cm. contained between plane parallel ends, and c is the concentration in gram molecules per litre of the absorbing substance. a or ϵ is a constant depending upon the substance considered and wave-length of the light employed, but apart from the exceptions mentioned below independent of c or d . If the thickness is maintained constant and the concentration varied, $\log \frac{I_0}{I}$ should be proportional to

the concentration (Beer's law). This law is frequently found to be invalid, especially in the case of electrolytes and at high concentrations, the deviations being due to a variety of causes such as changes in the degree of ionization, solvation, etc. Deviations from Lambert's

law (proportionality between $\log \frac{I_0}{I}$ and d) are much

rarer and their existence may generally be taken as indicating the occurrence of photochemical changes during the measurements; spurious deviations due to the use of non-parallel or impure light for the measurements may, however, be easily obtained.

From (1a) the absorbed light energy $(= I_0 - I) = I_0(1 - e^{-\epsilon cd})$, and this expression reduces to very easily used forms when ϵcd is very small or very large. If ϵcd is very large $e^{-\epsilon cd}$ approaches zero and the absorbed energy becomes equal to I_0 , and if ϵcd is very small $e^{-\epsilon cd}$ equals $(1 - \epsilon cd)$ and the expression for the absorbed energy becomes

$$I_0 - I = I_0 \epsilon cd.$$

If decadic logarithms are used the corresponding simplification is of course :

$$I_0 - I \propto I_0 \alpha cd \quad . \quad . \quad . \quad (2)$$

The constants here denoted by ϵ and α are known as the molecular extinction coefficients. There is, however, no settled usage as regards the symbol expressing the extinction coefficient, α, ϵ, k , etc., being used for the decadic coefficient by different authors.

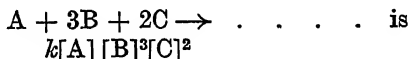
When two absorbing substances A and B are present together the absorbed energy is given by

$$I_0 - I = I_0 \{1 - 10^{(-\alpha_A C_A d - \alpha_B C_B d)}\}$$

provided that no interaction between A and B takes place, and the fraction of the total energy absorbed which is absorbed by one of them, A, is given by :

$$\frac{\alpha_A C_A}{\alpha_A C_A + \alpha_B C_B} \quad . \quad . \quad . \quad (3)$$

In the domain of pure chemical kinetics the laws connecting the rate of chemical change with the concentrations and temperature of the reacting substances have considerable bearing upon photochemistry. The law of mass action of Guldberg and Waage states that the rate at which a substance enters into chemical reaction is proportional to its active mass, which may in most cases be taken as being its concentration in moles per litre. Expressed symbolically the rate, i.e. the amount of chemical change in unit time, of the reaction



in which the square brackets represent the concentrations of the substances enclosed by them and k is a constant called the velocity constant, giving the rate of reaction when all the concentrations are unity.

k depends upon the absolute temperature, T , according to the relation due to Arrhenius

$$\frac{d(\log k)}{dT} = \frac{E}{RT^2}$$

where E is a constant having the dimensions of energy and R is the gas constant. Integrated this becomes :

$$k = Ze^{-\frac{E}{RT}} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The explanation of this equation is supplied by a consideration of the Boltzmann expression for the fraction of the total number of molecules which have each an energy content ϵ , namely $e^{-\frac{N\epsilon}{RT}}$ in which N is the number of molecules in a gram molecule. If now it is assumed that in a bimolecular reaction, reaction only occurs when two molecules contain energy greater by ϵ than the normal amount, E will be $N\epsilon$, the energy needed to cause the reaction of one gram molecule of each reactant, and Z the total number of collisions between the reactants in unit time in a volume of one litre, the concentrations of the reactants being one gram molecule per litre. Equation (4) has been verified within the experimental error for a number of gas reactions. E is known as the energy of activation and is characteristic of the reaction and not of the individual reactants. It can be determined experimentally as the slope of the curve obtained by plotting $\log k$ against $\frac{1}{T}$, after applying the small correction for the increase in the collision number, Z , with rising temperature.

It was natural that it should have been considered that the function of the light energy absorbed in photochemical processes was to supply the energy of activation necessary for reaction, but the absence of any idea

as to the manner in which the activation was brought about by light absorption, or the amount of energy thereby supplied to the individual molecules prevented any real advance, investigators usually confining themselves to fitting their experimental results to a modified mass law expression such as—

$$\text{rate of reaction} = k'I_0[A]^n[B]^m.$$

The advent of the quantum theory supplied the answer to these problems and completely revolutionized the study of photochemical kinetics, and a short résumé of its chief results of importance to the photochemist ensues.

QUANTUM THEORY

The origin of the quantum theory lay in the difficulty in which the classical electromagnetic theory of light found itself in attempting to explain quantitatively the spectral distribution of the energy radiated from a black body and the variation of the distribution with temperature. . Two formulæ had indeed been proposed, but while they were in agreement with experiment within certain restricted limits (Wien's formula when the product of wave-length and temperature was small and the Rayleigh-Jeans formula when this product was large), outside these limits they failed utterly to represent the facts.

A satisfactory solution of the problem was forthcoming, however, when Planck in 1900 by the introduction of revolutionary assumptions regarding the nature of radiation, and the manner of its absorption and emission by matter, deduced an expression which accurately reproduces the experimental data, and which reduces to the Wien and Rayleigh-Jeans expressions under the conditions in which these are valid.

These assumptions, as later modified, were that the absorption and emission of radiation is not a continuous process, but takes place in such a way that a given atom or molecule can at any moment only emit or absorb certain definite frequencies and, moreover, only

a certain finite quantity of energy of these frequencies. The quantity of radiant energy q which can be emitted or absorbed by a suitable atom or molecule is given by

$$q = h\nu \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where h having the dimensions of action (energy \times time, or momentum \times length) is known as the quantum of action, or the Planck constant, and has the value 6.55×10^{-27} erg-seconds, and ν is the frequency of the radiation. Not only can no smaller quantity of radiant energy of frequency ν than $h\nu$ take part in an energy exchange between matter and radiation, but also when larger quantities are involved they can only be integral multiples of $h\nu$. $h\nu$ is in radiation thus analogous to the atom of chemistry and is called the quantum of radiation. It is important to realize, however, that although with a given frequency the size of the quantum is constant, with changing frequency the size of the quantum changes in like manner. The accompanying Fig. 1 shows graphically the relation between the wave-length, λ , frequency (the reciprocal of the wave-length in cm.) and $Nh\nu$ (or the energy contained in a 'gram molecule' of quanta) in calories. The connexion between the last two is of especial importance owing to the frequent use of cm^{-1} as a measure of the quantity of energy $Nh\nu$.

Applications of this theory of the 'atomic' nature of radiant energy led to many important advances in physics of which the more important in relation to photochemistry were Bohr's atom model, and the deductions which have since been made with its aid. This atom model, though it has undergone very considerable modification, especially in the light of the recent developments of the quantum theory, still supplies a picture, suitable for many purposes, of the elementary changes wrought upon matter by the action of radiation.

In 1913 Bohr showed that, for the hydrogen atom, if the angular momentum of rotation of the electron

in its orbit around the nucleus were made to obey a relation similar to (5), namely, that its momentum could only have values given by $\frac{hn^1}{2\pi}$ where n is an integer, the spectrum of atomic hydrogen could be accounted for in its general structure. The limitation of the angular momentum proscribes the electron

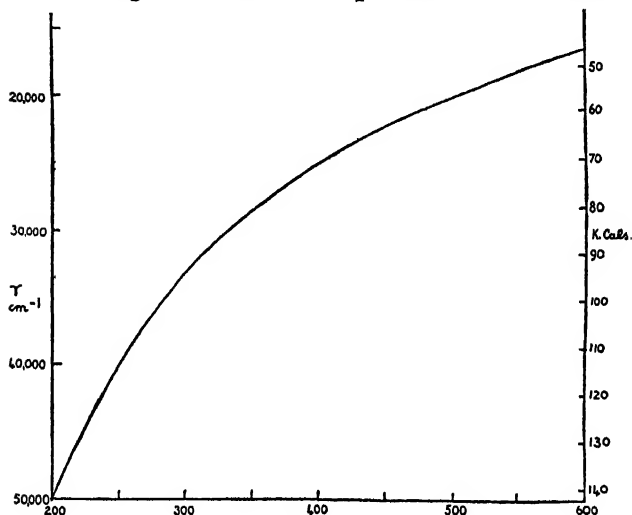


FIG. 1

from all but certain orbits whose radii, a , are given by

$$a = \frac{n^2 h^2}{4\pi^2 m e^2} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where e is the charge and m the mass of an electron ; while W , the total energy of the electron in any of these orbits, is given by

$$W = - \frac{2\pi^2 e^4 m}{h^2 n^2}$$

¹ This follows from the assumption of an 'atomicity' of action, the 'atom' being h .

the zero of energy being taken as that when the electron and nucleus are infinitely separated.

From these expressions it will be seen that the energy and radius of the electron orbit is completely defined when n —the quantum number—is known.

If now the electron changes from the orbit $n = n_1$, to another in which $n = n_2$, the energy content of the atom will have changed by the amount

$$\frac{2\pi^2 e^4 m}{h^2} \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right)$$

Assuming that the change in the quantum number is brought about by the absorption or emission of radiation, one quantum— $h\nu$ —of radiant energy will have been involved and this quantum must exactly equal the change in the energy content of the atom

$$\therefore h\nu = \frac{2\pi^2 e^4 m}{h^2} \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right)$$

$$\therefore \nu = \frac{2\pi^2 e^4 m}{h^3} \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right)$$

a relation which in the form

$$\nu = R \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right)$$

was already known empirically to express the frequencies of the spectrum of atomic hydrogen.

When atoms with more than one planetary electron are considered the problem becomes too complicated for treatment by ordinary methods, while in addition, the energy of an electron rotating in an elliptic orbit, which in the case of the hydrogen atom would equal that of the corresponding circular orbit, depends in all other atoms upon the eccentricity of the orbit. Nevertheless it is possible from an analysis of the spectra emitted and absorbed by these atoms, and by making use of certain rules, to determine the various permitted energy contents or energy levels of the atom

and to obtain some idea of the spacial distribution of the orbits and of the electrons among them.

To describe the energy levels of atoms other than hydrogen a single quantum number is found to be quite inadequate, it being necessary to introduce others, defining for example the eccentricity of the orbits and the energy of the electrons due to their spin or rotation upon their own axis.

Other atoms cannot, as can the hydrogen atom, change from any one energy level to any other, the rules, mentioned above, restricting, under normal conditions, the electronic system to but a few of the many possible transitions, although, when under the influence of a powerful field of force, lines corresponding to such normally forbidden transitions may be observed.

At ordinary temperatures and in the absence of any source of energy, such as high velocity electrons, all the electrons of practically every atom will be in the smallest possible orbits (since only a limited number of electrons can be present at one time in the same orbit, in general the electrons will not all be in the orbit of least diameter) and the energy content of the atom will be at its minimum---the normal state. By the absorption of energy, whether from radiation or some other source, the atom will be excited to higher levels, direct transition to which is not forbidden. If the source of the energy is continuous radiation, i.e. radiation containing all frequencies, it will have removed from it in passing through the matter those frequencies which correspond to possible electronic transitions. Mercury vapour for example so absorbs light of wavelengths 2537 Å and 1859 Å.

An atom which has been excited to some higher level than the normal cannot remain in the excited state indefinitely, but if it has not lost its excess energy either wholly or in part within a period, usually of the order of 10^{-7} to 10^{-8} second, must revert to some lower level, radiating the energy difference between the two levels as a fluorescence. For example, a mercury atom which has absorbed

a 2537 Å quantum can only revert to the normal state and will therefore radiate light of the same frequency as that originally absorbed. Absorption or emission lines of this nature are known as resonance lines.

In addition to loss of energy by re-radiation the atom can also revert to the normal state by transferring its energy to some other molecule with which it collides. Since the number of collisions undergone by any atom or molecule per second, in a gas at normal temperatures and pressures, is of the order of 10^9 to 10^{10} , it follows that, if this energy transfer occurs at any large proportion of the collisions all but negligibly few of the excited atoms will lose their energy in the collisions (be deactivated) and the fluorescence reduced to vanishingly small intensity. It is therefore only when the pressure is very low that all the absorbed energy will be re-emitted as fluorescence.

Experiments in which the intensity of the fluorescence of mercury and other vapours in the presence of varying pressures of foreign gases has been measured, show that the power to deactivate excited molecules varies considerably with different gases, and depends not only upon the nature of the added gas but also upon the nature of the excited atom. As a general rule oxygen is amongst the most efficient and the inert gases, especially helium, amongst the least efficient. In the case of excited mercury atoms oxygen is roughly three thousand times as efficient as helium, i.e. if every collision between excited mercury atoms and an oxygen molecule leads to deactivation of the atom only one in every three thousand collisions between helium and mercury does so. Even if it be assumed that every collision between oxygen and excited mercury leads to deactivation, the results obtained show, as might be anticipated from (6), that the collision diameter of the excited mercury is many times greater than that of the normal mercury atom, a result which must be borne in mind when reactions involving excited molecules are being considered.

Experiments in which mixtures of mercury and thallium vapours are exposed to monochromatic light of wave-length 2537 \AA , to which thallium vapour is completely transparent are of interest as showing the effect of the deactivation process upon the deactivating molecule. The fluorescence obtained from this mixture upon illumination contains many lines due to thallium, those thallium lines being most strong, which arise from the thallium energy levels nearest in energy content to that of the originally excited mercury atom, thus indicating that in a deactivating collision that process is most probable which leaves the maximum amount of the energy as energy of electronic motion and produces the minimum possible change in the kinetic energy of translation of the colliding particles. Inelastic collisions of this type, where electronic energy is degraded into kinetic energy of translation, or heat, are known as 'collisions of the second kind', while the reverse type in which translational energy is converted into electronic energy are termed 'collisions of the first kind'.

In an atom the only result of light absorption possible is to change the electronic energy, but when we come to consider di- and polyatomic molecules two other possibilities are introduced.

In the first place the molecule can rotate as a whole about its centre of gravity; and in the second, the atoms of the molecule can vibrate to and from one another, and although the energy involved in these motions is much smaller than that due to changes in the electronic levels, being respectively of the order of $1/100$ and $1/10$ of these, they exert a profound influence upon the nature of both the emission and the absorption spectra of molecules.

As in the simple hydrogen atom, the angular momentum of the electron is restricted to integral multiples of $\frac{h}{2\pi}$, so also is the angular momentum of the molecule as a whole similarly restricted, the only possible values

of the momentum being given by $\frac{m\hbar}{2\pi}$ and the energy of rotation by $\frac{\hbar^2 m^2}{8\pi^2 I}$ (m being the rotational quantum number and I the moment of inertia of the molecule). m is only permitted to change by ± 1 in absorption or emission so that the spectrum of molecular rotation which lies in the long infra red ($\lambda > 10\mu$) should consist of a series of lines separated by the constant frequency difference $\frac{\hbar}{4\pi^2 I}$. Actually owing to centrifugal expansion of the molecule and consequent increase in I , as the rate of rotation increases, the frequency separation of the lines decreases slightly as m increases.¹

When the short infra-red region of the spectrum ($\lambda = 1$ to 10μ), in which the vibration spectra lie, is examined a series of lines such as occur in the long infra red is not found but rather a series of bands, i.e. groups of lines. These bands originate in the simultaneous occurrence of changes in the energies of vibration and of rotation.

Confining our attention to diatomic molecules, an application of the quantum rules shows that if the vibration of the atoms of the molecule is simply harmonic the energy of the vibration is limited to integral multiples of $h\nu'$, ν' being the frequency of vibration. The vibrational energy can therefore be written as $p h\nu'$, where p is the vibrational quantum number. The simultaneous occurrence of change in the rotational energy, which may be increased or decreased, causes the appearance of absorption or emission lines whose frequencies are given by :

$$\nu = \nu_v \pm \nu_r$$

¹ Although the magnitude of the angular momentum of the electron in its orbit and of the rotation of the molecule as a whole are the same when the quantum numbers n and m are equal the energies of the electronic and molecular rotation will differ on account of the different moments of inertia, to which the energies are inversely proportional.

in which ν_v is the frequency of vibration and ν_r the frequency corresponding to the change in the rotational energy.¹

The emission or absorption of radiation can only be observed in the case of electrically unsymmetrical molecules (dipoles or heteropolar molecules), consequently the symmetrical homopolar diatomic molecules of the elements, e.g. chlorine, show no infra-red spectra. Changes in the electronic energy levels of the molecule may, however, disturb the symmetry and so make changes in the vibrational and rotational energies possible. It is to be noted, however, that in comparison with atoms the number of electronic energy levels which can be observed is very limited.

For the same reason that vibration bands are produced by changes in the vibrational energy, a change in the electronic energy level of a molecule does not cause a single emission or absorption line but a complex band system, made up of lines due to simultaneous changes in the electronic, vibrational and rotational energies.

The fractional number of molecules in any vibrational level of energy E per gm. molecule is given by the expression $e^{-\frac{E}{kT}}$, so that at sufficiently low temperatures the number of molecules in any but the lowest level can be neglected. If we now consider the absorption spectrum of a molecule under these conditions, the electronic band system will consist of a number of bands (each similar in nature to the infra-red vibration bands) due to the increase in the electronic energy plus the increase in the vibrational energy from that of the zero level of the normal molecule to that of any other level of the excited molecule; while

¹ The restriction rules do not permit in general of the occurrence of the frequency corresponding to $\nu_r = 0$, so that the line of frequency ν_v is missing from the bands. Also in the strictly simple harmonic vibrator p may only change by unity and consequently only one vibration band having its centre at $\nu = \nu_v$ would be observed, actually the vibrations are always anharmonic, and other bands due to changes in p of two or more may appear.

within each band will be the fine structure lines due to the simultaneous changes in the energy of rotation, the frequency of each of these lines being obtainable from the sum of the energy changes involved by the quantum relation; energy change = $h\nu$.

By sufficiently raising the temperature, an exactly similar series of bands due to changes of electronic and rotational energies combined with an increase in the vibrational energy from that of the first vibrational level of the normal to that of other levels of the excited molecule will be superimposed upon the first band series. This series of bands, therefore, will relatively to the other series be moved bodily towards lower frequencies through a distance corresponding to the energy difference between the zero and first vibrational levels of the normal molecule. At yet higher temperatures not only will band series due to the zero and first vibrational levels of the unexcited molecule be observed, but also series due to many of the higher levels. This is the case at ordinary temperatures.

A complete analysis of an electronic band spectrum enables the rotation and vibration levels not only of the normal molecule, but also of the excited molecule to be ascertained, and in addition, the law connecting the forces between the nuclei with their separation in both states of the molecule, and many other valuable data concerning the structure of the molecule. Apart from Raman spectra this is the only means whereby such data can be obtained for non-polar molecules.

Owing to the interference from the fields of neighbouring molecules and frequent occurrence of collisions between the molecules, the lines are considerably broadened, excepting when the total gas pressure is low. In solution, and indeed frequently even with quite moderate gas pressures the broadening is so extensive that the lines and bands are merged into a continuous absorption and completely lost. Hence, for the observation of rotational fine structure rather low pressures of gas are normally required.

If the vibration of the molecule were strictly harmonic, i.e. if the force restoring the atoms of the molecule to their equilibrium position were proportional to their displacement from it, the frequency difference between the bands arising from any one initial vibrational level would be constant. The law connecting force and displacement, however, contains terms involving the displacement raised to the second and higher powers—as a result of which the separation of the bands may increase or decrease with rising frequency. In some cases the law is such that as the vibrational quantum number of the excited state increases the band separation tends rapidly to zero. Following a series of bands due to such a molecule from low to high frequencies a frequency will finally be reached, at which all the higher vibration bands are superimposed, and beyond which no bands—at any rate arising from the same initial vibrational level—can be found. If this convergence limit of the bands can be observed it will be found that there stretches beyond it, towards higher frequencies, a more or less extensive region of continuous absorption, which no reduction of pressure or increase in the resolution of the spectrograph will break up into a band system. Such true continuous absorption, therefore, differs markedly from that mentioned above which could, under suitable conditions, be resolved.

The occurrence of a convergence limit in a band spectrum, accompanied by a region of true continuous absorption, is explained as being due to the dissociation of the molecule into its component atoms, the dissociation being just possible at the convergence limit, whose frequency apart from a correction discussed below gives the energy of dissociation of the molecule. In the continuous region the molecule is dissociated into atoms having kinetic energy of translation given by the difference in frequency between that of the light absorbed and of the convergence limit.

The convergence of a band system results from a

non-linear relation between force and displacement or, which amounts to the same thing, because the potential energy of the nuclei when their separation differs by x from the mean value is not proportional to x^2 but to some more complex function. The general shape of the curve of potential energy against the nuclear separation for a molecule which gives the type of band spectrum we are considering, is shown in Fig. 2, in

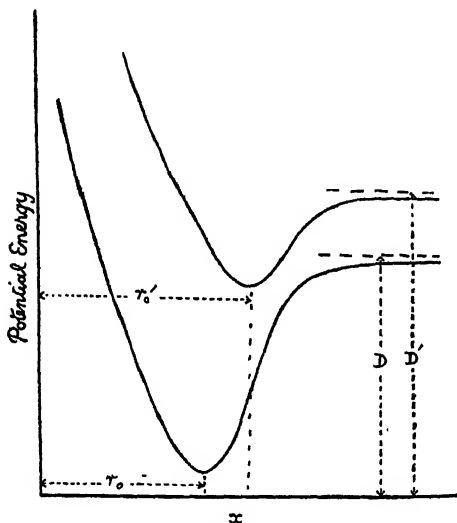


FIG. 2

which the lower curve applies to the normal and the upper to the excited molecule, r_0 and r'_0 being the respective equilibrium separation of the nuclei. As the separation increases indefinitely the curves approach the dotted lines asymptotically, which therefore represent the maximum energies which the molecule can contain, the access of any larger amount causing dissociation within a time approximating to the period of vibration or roughly 10^{-13} second.

D is thus the energy of dissociation of the normal molecule. D' is the energy corresponding to the convergence limit and is greater than the heat of dissociation of the normal molecule on account of the electronic excitation of the molecule, which causes it to dissociate not into two normal atoms, but into one normal and one excited atom. $D'-D$ is therefore the energy of excitation of this atom, and if this quantity can be determined in any way, e.g. from the emission spectrum of the atom, the heat of dissociation of the normal molecule can be calculated from the frequency of the convergence limit.

In the case of the completely polar molecules such as alkali halides, etc., the transfer of the electron from the electro-negative to the electro-positive atom may take the place of the atomic excitation of homopolar molecules ($D'-D$) then = 0, and the convergence limit gives the thermal heat of dissociation directly.

It is to be noted (1) that it is the increase in the vibrational energy which causes the dissociation, the electronic excitation serving merely to make the molecule capable of absorbing the necessary light energy, since with homopolar molecules radiation is not capable of changing the vibrational energy of the normal molecule, while even with heteropolar molecules the intensity of absorption at frequencies capable of raising the molecules to the higher levels becomes vanishingly small; (2) that a heat of dissociation so determined is that which would be obtained calorimetrically at the absolute zero of temperature, this because the convergence limit used for the calculation is that of the zero vibrational level, whereas the heat of dissociation found by other means is the weighted mean of the heats of dissociation of all the vibrational levels present at the temperature of the measurement.

Table I shows some of the heats of dissociation of which use will be made later; both the thermal and optical values are given in order that a comparison may be made between them. In the case of oxygen

the optical value is certainly by far the more reliable, while in the case of the hydrogen halides it is the less certain.

TABLE I

(Heat of Dissociation.)			(Heat of Dissociation.)		
Substance.	Optical. Cals.	Thermal. Cals.	Substance.	Optical. Cals.	Thermal. Cals.
O ₂ .	128,000	250,000	I ₂ .	35,200	35,100
H ₂ .	101,000	circ. 100,000	HCl .	130,000	101,000
Cl ₂ .	58,500	57,000	HBr .	97,500	84,500
Br ₂ .	45,200	46,200	HI .	64,500	69,000

Confirmation of the occurrence of such adiabatic dissociation of molecules by light (dissociation occurring directly as a result of light absorption without the intervention of a collision), has been obtained with the halogens and hydrogen, the methods being, for hydrogen the demonstration of a fall in the pressure upon illumination with light of short enough wave-length, due to the adsorption of the atoms upon the walls of the vessel; and for the halogens the demonstration of an increase in the thermal conductivity of the gases upon illumination. Experiments with the halogens showed further that in accordance with theory no measurable dissociation was produced by wave-lengths greater than the convergence limit, at any rate under the conditions prevailing during the experiment. Photochemical evidence, which we will consider later, indicates, however, that at higher pressures dissociation may occur in light of longer wave-lengths.

As with excited atoms, an excited molecule cannot retain its energy indefinitely, but must lose it by collision with another molecule, or if this does not occur within the life of the excited state (10^{-7} to 10^{-8} sec.) the absorbed energy must be re-radiated as fluorescence. This affords further evidence of photo-dissociation with wave-lengths shorter than that of the convergence limit, for although iodine vapour at low pressures exhibits a strong fluorescence when illuminated by longer wave-length light, no fluorescence can be detected

when wave-lengths shorter than the convergence limit are employed.

Though the above is strictly true of diatomic molecules, the adiabatic dissociation of polyatomic molecules can occur as a result of absorption of light within a region of banded absorption.

In polyatomic molecules the several atoms present can vibrate in a number of ways, each of which will have its own frequency. The band spectra are therefore much more complex than those of diatomic molecules.

It is found that in the electronic band spectra of polyatomic molecules there is often a more or less definite frequency below which the individual rotation lines are clearly defined, but above which these lines have merged together, each band having become a narrow region of continuous absorption. Owing to the numerous vibrational degrees of freedom of these molecules, it is possible for a quantum of energy greater than that capable of dissociating the molecule into two parts, to be absorbed without producing dissociation, if this energy is distributed among the various degrees of freedom. If now, at some time subsequent to the absorption process a redistribution of its energy takes place within the molecule, so that the dissociable degree of freedom receives sufficient to disrupt the linkage concerned, dissociation may follow.

The accepted explanation of the sudden disappearance of the rotation lines in polyatomic band spectra is that this redistribution of energy followed by dissociation has occurred. The continued quantization of the vibration after the disappearance of the rotation lines further shows that the time interval between the absorption of the quantum and the redistribution of its energy, lies between the periods of rotation and vibration or 10^{-13} to 10^{-12} seconds. Band spectra of this type are known as predissociation spectra and have been observed with a number of substances, including nitrogen peroxide, ammonia, benzaldehyde and acetaldehyde.

In solutions and the denser phases generally, as already mentioned, the lines and bands of a band system become merged into continuous absorption. (Certain benzene derivatives, however, show when dissolved in solvents such as hexane a modified band spectrum.)

The continuous absorption in these denser phases frequently possesses an extinction coefficient which at first rises with decreasing wave-length, then passes through a maximum and decreases. The maximum value of the extinction coefficient, the wave-length at which it occurs and general shape of the extinction coefficient wave-length curve, though varying somewhat from substance to substance and with the solvent are characteristic of the particular group of atoms (or rather the valency electrons holding them together) responsible for the absorption, e.g. the bands of the nitrate ion and carbonyl group. Such bands being continuous little use can be made of them to determine heats of dissociation or other properties of the molecule, but if the group of atoms responsible for the absorption can be identified this knowledge may be of considerable assistance in deciding the mechanism of a photochemical process.

Before concluding this summary, reference must be made to the fluorescence observed with solutions of certain organic dyes and other substances, usually of rather complex structure. If the solution is very dilute a fraction of the absorbed light energy, not far short of unity, is re-emitted within about 10^{-7} to 10^{-8} seconds after the absorption, as fluorescence. As the concentration of the fluorescent substance is increased the ratio $\left(\frac{\text{fluorescent energy}}{\text{absorbed energy}} \right)$ decreases rapidly, a decrease which can also often be brought about by the addition of other substances to the solution. This is due to the increasing frequency of collisions between normal and excited molecules of the dye, collisions which are able to deactivate the excited molecule and

so prevent the re-radiation. The high efficiency of the fluorescence in dilute solution is important as showing that these excited dye molecules must be exceedingly stable with regard to collisions with solvent molecules of which at least hundreds must occur in the interval between the absorption of the quantum and its re-emission.

The theoretical connexion between the amount of photochemical change and the absorbed radiant energy is given by the law of the photochemical equivalent originally deduced by Einstein by means of thermodynamic reasoning in 1905, but although Stark and others also drew attention to the importance of the quantum theory to photochemistry, little use was made of it till Einstein in 1912 re-deduced his equivalence law from a consideration of the Bohr atom model.

This law states that, under the conditions implicated by the deduction, one light-absorbing molecule should react for each quantum of radiation absorbed.

For a molecule excited by light to a higher electronic energy level two courses are open: (*a*) it may lose its absorbed energy by fluorescence, deactivation, etc., or (*b*) it may undergo chemical change owing to its excitation. If now (*a*) is of very rare occurrence compared with (*b*), every excited molecule will react, and each absorbed quantum will lead to the reaction of one molecule, provided that no secondary chemical changes take place.

The publication of the second deduction stimulated a large volume of experimental work testing the validity of the law and the conditions under which it could be applied. Now the energy of activation needed for thermal reactions usually corresponds in amount to a quantum of short infra-red radiation, and it was accordingly suggested that thermal reactions were photochemical in origin, the activation being due to the absorption of infra-red radiation of the correct frequency from the normal temperature radiation

present in the system. Although this theory had much to commend it, and apparent confirmation of it was forthcoming by the discovery in certain cases of absorption bands at about the right frequency, it has had to be discarded owing to numerous difficulties, among which may be mentioned the absence of any known reaction (apart from some reactions of iodine taking place in the very short infra-red, which are easily accounted for) which is accelerated by exposure to intense infra-red radiation. Indeed, it appears that photochemical reaction can only be produced when the electronic system of the absorbing molecule is suitably excited, the production of an increase in the vibrational or rotational energies alone, by light, being incapable of leading to chemical change.

So far as the initial activation is concerned, therefore, thermal and photochemical processes will in general differ. In some cases this difference is inessential and is no bar to identical behaviour and mechanisms for a reaction which is capable of occurring both thermally and photochemically. In other cases the difference is far reaching, as, for example, the decomposition of hydrogen iodide, which thermally proceeds by way of collisions between activated molecules, whereas the photodecomposition is, as will be seen later, due to the formation of free atoms. Not infrequently the thermal and photo reactions of the same system are quite different.

In addition to the variables which must be considered in the investigation of thermal reactions : concentration, temperature, effect of changes in the solvent medium, surface, effects, etc., the photochemist must also take account of the effects of intensity, wave-length, and degree of monochromatism of the light he employs.

CHAPTER II

THE PRIMARY LIGHT PROCESS

IN the previous chapter reasons were given for believing that a molecule which has absorbed a quantum of visible or ultra-violet radiation is either raised to a higher electronic level or dissociated, and the method whereby it can be decided which of these alternatives will occur under any particular set of conditions was indicated. The chemical changes which may succeed upon these purely physical processes depend upon a variety of factors and may be exceedingly complex. In the present chapter, however, only those reactions will be considered in which the chemical processes following the light absorption are fairly simple and afford to some extent a measure of the absorbed light energy, and a means of testing the Einstein photochemical equivalence law. Those reactions involving complicated secondary chemical changes, the mechanisms of which are often very uncertain, will be left till later.

In any discussion of the photochemical equivalence law a sharp distinction must be drawn between the physical and the chemical fulfilment of it. When an isolated molecule absorbs a quantum the formation of an excited molecule or its dissociation is the invariable result, and thus limited, the law is absolutely valid. Its chemical validity, however, depends upon the chemistry of the succeeding processes which in turn depend upon a number of factors, both chemical and physical, which may reduce the chemical yield below the theoretical value of unity or raise it to some higher value.

The observed chemical changes will be due to the reaction of the excited molecule or the dissociation products formed by the light, and will occur only when the conditions are favourable to reaction, in a bimolecular reaction, for example, when a collision takes place between

the light-activated ¹ molecule and a molecule with which it can react, and any factor which reduces the frequency of such collisions will tend to reduce the chemical yield.

Below are enumerated the chief physical causes of reduced yields :

(1) In a gas at normal temperature and pressure each molecule undergoes every second about 10^{10} collisions with other molecules and in solution or the liquid state this number will probably be considerably augmented. When the molecules are not all of one kind—as in a solution or mixture of gases—these collisions will be divided among the various kinds of molecules present, roughly in proportion to their concentrations. If a reaction is one between photo-excited molecules of one sort with molecules of some other sort, the activated molecule will not in general collide at once with a molecule with which it can react but will first meet with a number of other molecules, depending upon the relative concentrations, in collisions which will not only be unproductive of reaction, but even able to deactivate the excited molecule. If enough of its energy is removed in this way the excited molecule will be incapable of reaction when an otherwise favourable collision does occur.

If to a mixture of two gases, which react photochemically in the above manner, is added a third inert gas, the number of molecules which react per absorbed quantum (the quantum yield denoted by γ) will decrease as the partial pressure of the inert gas is increased. As has been shown to be the case with excited mercury atoms different gases will not be equally efficient in reducing the quantum yield; an efficient deactivator

¹ Activated is used here and in the sequel to designate any molecule which has received sufficient energy from any source whatever to make it chemically reactive. This energy may be contained in any degree or degrees of freedom of the molecule, or may be used to dissociate it. Activated molecules produced by light will be electronically excited or dissociated molecules, but this will not necessarily be the case with other sources of energy.

will reduce the yield appreciably when its partial pressure is small, while one that is inefficient may produce no measurable change even at high partial pressures.

In solutions, especially when dilute, where the ratio of the collision rate between excited and other reactant molecules to that between excited and solvent molecules is small, the quantum yield will be very low unless the excited molecules show particular stability to collisions with molecules of the solvent.

When the absorbing substance is dissociated adiabatically by light, deactivation processes should be negligible in the gaseous phase owing to the great difference between the duration of the dissociation process (10^{-13} sec.) and the interval between successive collisions (10^{-10} sec. at N.T.P.), but in the liquid phase they may play an important part.

Since the deactivation process can cause the activation of the deactivating molecule (by collisions of the first kind) chemical activity may be induced in one molecule by the energy originally absorbed by another. This is known as photosensitization and will be discussed in greater detail later.

(2) The life of an excited molecule being usually of the order of 10^{-7} to 10^{-8} seconds, failure to encounter within this period of time a molecule with which it can react will mean that if the excited molecule has not already undergone a deactivating collision it must re-radiate its excess energy as fluorescence. Loss of energy through fluorescence is not likely to be an important factor controlling the quantum yield at normal pressures, but as the pressure is reduced to a point at which the time interval between successive collisions of excited molecules with reactant molecules becomes comparable with the mean life of the excited state a fall in the yield accompanied by the appearance of a fluorescence is to be anticipated in all reactions in which excited molecules take part.

An important application of this has been made to

the photo decomposition of ammonia gas in light of wave-length about $200m\mu$, in which region of the spectrum it shows banded absorption. The decomposition was accordingly considered to involve excited ammonia molecules. The quantum yield did not, however, decrease at low pressures in the manner to be expected if this were the case and a closer examination of the absorption spectrum proved it to be of the predissociation type, thus suggesting that dissociation of the ammonia molecule actually occurred.

The causes of quantum yields greater than unity are mainly chemical, and together with the chemical processes tending to reduce the yield, provide the chief source of interest in photochemistry to the general chemist and will therefore be discussed in some detail.

Photochemical reactions can be divided into two types, those in which excited molecules take part, and those in which reaction is due to the products of a photo-dissociation.

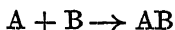
DISSOCIATION TYPE

Great interest centres around this type of reaction on account of the insight it provides into the chemical properties of atoms and free radicals.

If a molecule AB is dissociated into its constituents $A + B$ these atoms or radicles which have an 'unsaturated valency' will be exceedingly reactive and will react with great readiness with any other molecules, say X and Y, with which reaction may be possible:



If, however, these reactions are slow, i.e. if they only occur with a small proportion of the collisions between the reactants owing to the necessity of a large preliminary thermal activation, the reverse of the dissociation process,



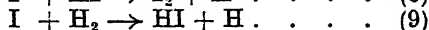
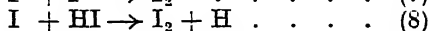
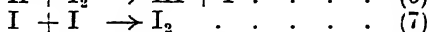
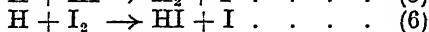
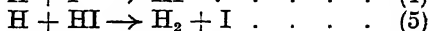
may take place to an appreciable extent before (1)

and (2) can occur and the quantum yield be correspondingly reduced.

A gas reaction of this type showing very simple behaviour is the decomposition of hydrogen iodide into hydrogen and iodine. The quantum yield has been determined for the three wave-lengths 207, 253 and $282m\mu$, being equal in each case to 2 within the experimental error. (The quantum yield is always expressed—photo-sensitized processes excepted—in terms of the number of molecules of the light-absorbing or photo-sensitive reactant, in this case HI.) This figure is scarcely affected by change of pressure between 0.1 mm. and atmospheric, or by change of temperature throughout the range studied, while the addition of nitrogen up to a partial pressure of at least $3\frac{1}{2}$ atmospheres is also without effect. Even in the liquid state the yield only falls to 1.84.

Gaseous hydrogen iodide absorbs continuously under all conditions below about $300m\mu$, and must therefore be dissociated into hydrogen and iodine atoms. No trace of the banded absorption spectrum which would be anticipated at higher wave-lengths has been found and it must be concluded that the absorption of such wave-lengths is so weak as to elude detection.

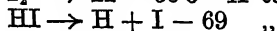
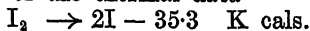
To explain the quantum yield of 2, the substances present in the insulated system and the ways in which they can react with atomic hydrogen and iodine must be considered. After the insolation has been in progress for a short time there will be present, hydrogen iodide at a high concentration, molecular hydrogen and iodine at low concentrations, and atomic hydrogen and iodine at very low concentrations. This being so, the following reactions are possible :



These will not, however, be all equally probable; indeed, many of them will be so improbable that they may be neglected: this for two reasons. Firstly because, when the concentration of both the reactants is very small, collisions between them will be of very rare occurrence compared with collisions between either of them and the other molecular species present. Accepting for the moment the rough gradation in the concentrations given above, the frequency of collisions capable of leading to reaction according to (5), (6) and (3) will decrease in this order. Secondly, thermodynamic, or thermal criteria can be called upon to show that certain of the reactions will take place at only a very small fraction of the total number of collisions between the reactants and these reactions can therefore generally be neglected.

As an endothermic reaction can only occur when the reacting molecules contain at the moment of the collision a quantity of energy at least equal to the energy absorbed in the reaction, at the best, only the fraction $e^{-\frac{Q}{RT}}$ of the total number of collisions can be productive. (Q equals the heat absorbed per gram molecule reacting.) With quite small values of Q this fraction becomes exceedingly small (excepting at high temperatures), and will be still further reduced in the event of additional thermal activation in the Arrhenius sense being needed. Highly endothermic processes can therefore be neglected.

Application of the thermal data



shows that reactions (8) and (9) are endothermic to the extent of 34 and 32 K cal. respectively and can therefore be ignored, but that the remainder are all thermally possible.

Reactions (3) to (6) all destroy atomic hydrogen and since (8) and (9) do not occur, the only way in which it is formed is by the photo-dissociation.

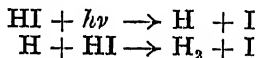
Its concentration will therefore become constant when its rate of removal by reactions (3) to (6) equals its rate of formation by the dissociation process. The existence of such a stationary concentration will be only possible if the concentration of the substance is small and the time needed for the attainment of equilibrium negligible compared with that needed for an appreciable change in the concentrations of the main reactants, —HI, etc.

There are good reasons for believing that reactions (5) and (6) occur at practically every collision between the reactants and as therefore practically every molecule with which it collides will be one with which an atom of hydrogen will react, its rate of removal will be very rapid and its concentration correspondingly very small.

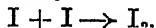
The concentration of atomic iodine although it is decreased only by (7) and increased by (5) and (6) in addition to the photo-dissociation will for similar reasons reach a constant value which, though small, will be higher than that of atomic hydrogen, owing to its greater rate of formation and lesser rate of removal.

Finally, as only a small percentage of the hydrogen iodide was decomposed in the investigation the concentration of iodine molecules was always small compared to that of hydrogen iodide.

Consequently of reactions (3) to (6), (5) will be by far the most frequent of occurrence, the others contributing scarcely at all to the final result, and we conclude therefore that there occur in the illuminated gas only the reactions :



followed in due course by

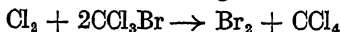


The quantum yield of two is thus readily accounted for, and it only remains to point out that should the iodine concentration become appreciable, the occurrence of reaction (6) in which hydrogen iodide is reformed

would reduce the yield, while if (8) took place at an appreciable fraction of the collisions between iodine atoms and hydrogen iodide molecules the yield would be increased. The demonstration of an inhibiting effect of iodine has proved difficult owing to the partial absorption of the active light by the iodine (internal filter) and although a reduction in the quantum yield was actually found when iodine was added, it is doubtful whether this cannot be explained as being entirely due to the internal filter action.

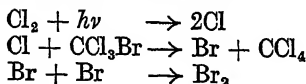
Although the majority of reactions that have been investigated have quantum yields of the order of unity, in but few is the yield so independent of the experimental conditions or the explanation of its value so well established, and indeed in many cases the conditions of experiment have been varied over too narrow a range to inspire any great confidence in either the actual value of the yield or the mechanisms proposed to account for it.

In the liquid phase an apparently simple reaction is that occurring between chlorine and trichlorobromomethane (CCl_3Br) both when pure or when dissolved in carbon or silicon tetrachlorides. It is here found that for each quantum absorbed very nearly one molecule of chlorine reacts according to the equation:



and the quantum yield is therefore very close to unity, at any rate within the range of wave-lengths 407 to $449m\mu$, with each of which wave-lengths the reaction has been investigated. The yield is unaffected by temperature change or by very considerable dilution with SiCl_4 or CCl_4 provided that these are quite pure.

These results are in accord with the scheme:



this being more in line with modern thought than the suggestions of the original investigators that excited

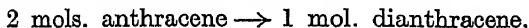
chlorine molecules took part, a proposal which has difficulty in explaining the maintenance of a yield of close to unity when the ratio $\frac{[\text{CCl}_4]}{[\text{CCl}_3\text{Br}]}$ is as great as 80.

ACTIVATED MOLECULE TYPE

The reactions just considered owe their simplicity in part to the rapidity of the dissociation process and consequent infrequency of collisions deactivating the primarily formed excited molecules. In reactions involving excited molecules, however, these may suffer many, possibly deactivating, collisions before meeting a molecule with which they can react, and in consequence the quantum yield may be expected to show a dependence upon the concentrations of the substances present, especially if one or more of these is merely a diluent or solvent and takes no direct part in the chemical change; while at low concentrations the limited life of the excited state will make itself felt owing to the loss of energy by fluorescence before reaction can occur.

Although a completely satisfactory explanation of its behaviour has not yet been produced, the polymerization of anthracene in solution may be cited as a reaction in which excited molecules almost certainly take part, and which also illustrates the above dependence of the quantum yield upon the concentration.

When exposed to ultra-violet light, which it absorbs strongly, anthracene undergoes the change



the dianthracene reverting to the simpler molecule in the dark.

The quantum yield is independent of temperature, and its variation with the anthracene concentration exhibits similar behaviour in a number of organic solvents such as phenetole, benzene, etc. As the concentration is increased from a very small value the yield also increases, though less and less rapidly than the concentration as this becomes higher, the yield

finally attaining a steady value at about 0.1 molar anthracene, beyond which further increases in the concentration do not affect the yield. Concurrently with the rising quantum yield the intensity of the fluorescence strongly emitted by dilute solutions steadily decreases, becoming imperceptible at approximately the same concentration as that at which the yield first attains its limiting value.

Fig. 3 indicates the relation between the velocity, which under the conditions of experiment was pro-

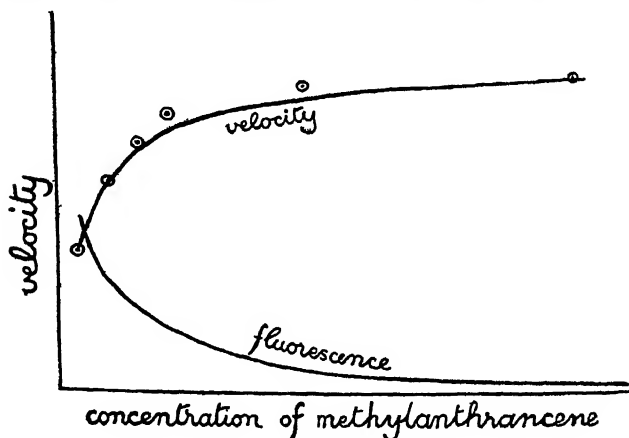


FIG. 3

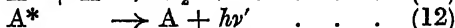
portional to the quantum yield and the intensity of the fluorescence and the concentration, the points being obtained actually with methylantracene.

The existence of this fluorescence at once suggests that excited molecules are formed as a result of light absorption and the other observations, a competition between fluorescence and chemical change for the absorbed energy.

The simplest mechanism for the process is deduced below, but while it satisfactorily accounts for the observed trend of γ with rising concentration, it leads to

a maximum value of unity, whereas the experimental figure is about 1/4, a discrepancy which is not entirely removed by the more complicated mechanism which has been suggested.

If A is the molecule of anthracene, A₂ dianthracene and A* an excited anthracene molecule, the processes in which they may take part are :



where ν' is the frequency of the quantum of fluorescent radiation.

A* is formed by (10) and destroyed by (11) and (12), and since its concentration is small it will soon reach a steady value when its rates of formation and destruction are equal.

$$\therefore k_{10}I_{\text{abs.}} = k_{11}[A][A^*] + k_{12}[A^*] \quad . \quad (13)$$

in which $I_{\text{abs.}}$ is the rate of absorption of energy and k_{10} , k_{11} and k_{12} are the respective velocity constants of the processes (10), (11) and (12). It is, of course, essential that $I_{\text{abs.}}$ and the concentrations be expressed in consistent units if the full significance of the constants is to be apparent, a point of less importance here than elsewhere. Such consistent units would be $I_{\text{abs.}}$ in quanta/unit volume/unit time and the concentrations in molecules/unit volume. In the present case using these units k_{10} will be unity if every absorbed quantum produces one excited molecule.

Solving (13) for $[A^*]$ we obtain

$$[A^*] = \frac{k_{10}I_{\text{abs.}}}{k_{11}[A] + k_{12}} \quad . \quad . \quad . \quad (14)$$

and substituting (14) in (11), we find the rate of formation of dianthracene :

$$+ \frac{d[A_2]}{dt} = \frac{k_{10}I_{\text{abs.}}[A]}{[A] + \frac{k_{12}}{k_{11}}}$$

$$\text{or } \gamma = \frac{\text{rate of reaction}}{I_{\text{abs.}}} = \frac{k_{10}[A]}{[A] + \frac{k_{12}}{k_{11}}} \quad (15)$$

This expression gives, when $[A]$ is small compared with $\frac{k_{12}}{k_{11}}$, a quantum yield rising with the concentration

and a constant value of γ when $[A] > \frac{k_{12}}{k_{11}}$. The curve so calculated for suitable values of the constants is shown in Fig. 3.

No account has here been taken of the possibility of deactivation by solvent molecules, an omission which can be justified by the close similarity of the results obtained in different solvents, it being unlikely that the deactivating power should be so completely independent of the deactivating molecule unless it were practically zero, and also by analogy with other complex fluorescing molecules with many of which solvent deactivation plays only a small part.

A gaseous reaction showing rather similar characteristics which is supposedly due to excited molecules is the decomposition of ozone. This gas possesses two regions of banded absorption, one in the red, and a second extensive region in the ultra violet of maximum intensity at about $255m\mu$. Absorption of light in both regions causes decomposition.¹

The kinetics of the decomposition and the effects of added gases show many points of similarity in both the visible and ultra-violet bands—the addition of a gas chemically inert towards ozone producing in all cases a reduction in the yield.

In red light the curve obtained by plotting γ against the partial pressure of oxygen closely resembles that

¹ The fine structure of these bands does not appear to have been investigated, and as the more recent values of the heat of dissociation are small enough to permit of the dissociation $O_3 \rightarrow O_2 + O$, even in red light the possibility of this primary process must not be overlooked.

obtained when the intensity of the fluorescence of iodine vapour is plotted against its pressure, indicating a deactivation of excited ozone molecules by oxygen. These curves are shown in Fig. 4, from which it will be seen that at low pressures γ has a constant value of about 2. The iodine fluorescence curve is plotted upon an arbitrary scale.

The addition of other gases also reduces the yield,

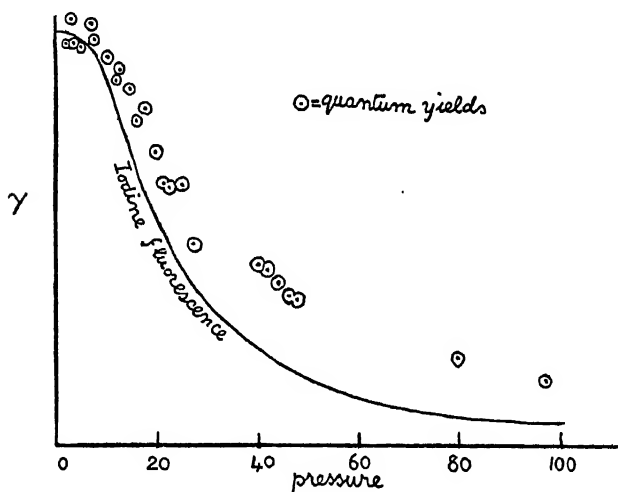


FIG. 4

though at the same partial pressure to a smaller extent than does oxygen. Under conditions otherwise constant the effect of these additions is given by the empirical expression:

$$\gamma = \frac{K}{k + \alpha[M]} \quad . \quad . \quad . \quad (16)$$

in which k and K are constants independent of, and α a constant dependent on, the added gas, $[M]$ being its concentration. α is apparently independent of wave-lengths at any rate to a first approximation and

for nitrogen and helium respectively, equals approximately 0.25 and 0.15.

A comparison of (15) and (16) might suggest by analogy that the added gases play the same part in ozone decomposition as does the anthracene concentration in its polymerization; too close a reliance upon such deductions would, however, be unwise. An examination of all the experimental data shows that this reaction is more complex than the selection given here would appear to indicate, and it is possible that future investigation may show that atomic oxygen takes part in the ozone decomposition.

To decide whether excited molecules play any essential part in a reaction mechanism the following should be investigated.

(1) The nature of the absorption spectrum under conditions favourable to the development of a banded spectrum and especially with polyatomic molecules, of the rotational fine structure;

(2) The existence of fluorescence of the absorbing molecule;

(3) The effect of the addition of chemically inert substances and in the case of a gaseous reaction, especially highly electro-negative gases, whose deactivating power is usually greater than that of the rare gases;

(4) The dependence of the yield upon the partial pressures of the reactants at low partial pressures.

The elucidation of the reaction mechanism will normally require a thorough investigation of the effects of temperature, light intensity and concentrations (or partial pressures) of the reactants, while change of wave-length and shape or size of the reaction vessel will also often throw valuable light upon the problem.

PHOTOSENSITIZATION

It is sometimes found that it is possible to cause a photochemical reaction to take place in light of a wave-length not absorbed by any of the reactants, if some other substance which does absorb this wave-length

is added to the system. Reactions brought about in this way are said to be photosensitized and the light absorbing but non-reacting substance is known as the photosensitizer.

The explanations of the known examples of this phenomenon fall mainly under two heads according as to whether the direct result of light absorption is the excitation of the sensitizer to a higher electronic level or its dissociation. In the first case reaction is induced by a transfer of the energy of excitation to a molecule of one of the reactants in such a way as to activate it for chemical change, and in the second case, the products of dissociation catalyze the chemical change in a manner analogous to that assumed in the intermediate compound theory of catalysis.

Probably the best studied examples of sensitization by excited molecules are those brought about by mercury vapour which has absorbed its 2537 Å resonance line. Evidence for the occurrence of a transfer of energy between excited mercury atoms and other atoms or molecules as shown by the fluorescence of thallium vapour induced by excited mercury atoms, has already been mentioned.

The energy of the quantum of $\lambda 2537$ equals about 112,000 calories per molecule, and provided that only a small proportion of this energy is degraded during the transfer to hydrogen, molecules of this gas should be readily dissociated, since the heat of dissociation is about 101,000 calories. Actually, hydrogen containing traces of mercury vapour, develops, when illuminated by the mercury resonance line, the properties to be expected from the presence of atomic hydrogen. These properties include the power of reducing many metallic oxides and unsaturated organic substances, and of combining with oxygen to form hydrogen peroxide, all at the ordinary temperature. In the absence of hydrogen many organic substances such as hydrocarbons, and inorganic substances such as ammonia, may be decomposed or oxidized if oxygen is present.

It is interesting to note that the quantum yields of these photosensitized processes are frequently many times greater than that of the direct photochemical reaction even when wave-lengths shorter than 2537 Å are used. The mercury sensitized decomposition of ammonia has, for example, a yield of about thirty times greater than that of the direct photo-decomposition occurring with a wave-length of about 2100 Å.

Fluorescent organic substances and the strongly fluorescent uranyl salts are also capable of photosensitizing some reactions, the former for example being used to sensitize the autoxidation of benzaldehyde to visible light and uranyl salts for the sensitized decomposition of some organic acids of which that of oxalic acid is noteworthy. Like the polymerization of anthracene, there exists here an inverse relation between the intensity of the fluorescence and the quantum yield,¹ the latter increasing as the concentration of oxalic acid approaches that of the uranyl salts, becoming unity when the concentrations are equal. Examination of the absorption spectra leads to the conclusion that a complex between the uranyl salt and the oxalic acid is formed and that light absorbed by the complex is alone capable of leading to decomposition. Here again the absorbed energy is more efficiently utilized in the sensitized than in the direct photo process, the yield of the latter being only 1/100 of a molecule per quantum at the shortest wave-lengths employed.

Direct contact between the sensitizer and the reactant is apparently also necessary if the photographic emulsion is to be made sensitive to wave-lengths unabsorbed by the silver halide, since only when the dyestuff is actually adsorbed upon the silver halide particle does the emulsion become sensitive to the region of the spectrum absorbed by the dye.

¹ It should be remarked that such a connexion between fluorescence and chemical change is far from being of general occurrence, the two examples given here being exceptional.

In nearly all known instances of photosensitization due to dissociation of the absorbing molecule the sensitizer is a halogen. An example which has attracted considerable attention is the chlorine sensitized decomposition of ozone, a reaction whose mechanism is at first sight seemingly simple since the quantum yield remains close to two with considerable variations in the experimental conditions. The simplicity is, however, apparently illusory, the decomposition proceeding through the intermediary of oxides of chlorine, of which evidence for the formation of ClO_2 has been brought forward, while by some authors the transient existence of ClO has been postulated. The bromine sensitized decomposition of ozone is possibly of greater complexity since higher oxides of bromine are formed and the surface of the reaction vessel plays an important part. Measured quantum yields in the neighbourhood of 30 have been obtained.

Another reaction sensitized by bromine in which high quantum yields prevail is the transformation of fumaric acid and its esters into the maleic isomers, quantum yields of over a thousand having been obtained under favourable conditions.

An iodine sensitized reaction which may be mentioned owing to its importance in iodimetry is the oxidation of solutions of hydriodic acid by free oxygen which takes place in visible light when iodine is present.

Before concluding this short section mention must be made of zinc oxide as a sensitizer, chiefly for oxidations of some organic substances and for certain reductions. It is presumed that the absorbed quantum produces an electric moment in the molecule of oxide, at which an electrolysis then occurs.

CHAPTER III

SECONDARY CHEMICAL PROCESSES, CHAIN REACTIONS

IN many photochemical processes the quantum yield attains to large figures—up to a million molecules per quantum have been observed—and consequently the chemistry of the processes succeeding the primary result of the absorption of a quantum must play an even more significant part than in the reactions so far considered. Before proceeding further, the characteristics, other than the large quantum yield, which may be exhibited by these reactions, and which serve to distinguish them from those having a simpler mechanism, will be enumerated.

1. There is usually a dependence of γ upon the concentrations of the reactants and often also of the resultants.

2. Traces of impurities may increase (positive catalysts) or decrease γ (inhibitors or negative catalysts), the latter effect especially being an almost certain indication of the existence of a 'chain reaction'.

3. Change of temperature or wave-length of the incident light may produce pronounced changes in γ .

4. Another almost certain indication of the presence of a chain reaction is a lack of proportionality between the velocity of reaction and the incident light intensity.

5. The stoichiometric reaction must be *exothermic*, although the converse statement that all exothermic reactions have high quantum yields is far from the truth. This follows from the fact that in an *endothermic* process the energy absorbed is supplied by the light quantum which would normally be sufficient for the reaction of only very few molecules.

A high quantum yield at once necessitates that either a number of simultaneous reactions be induced by the absorbed quantum, or else a series of consecutive

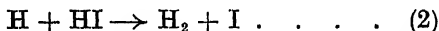
reactions succeed that occurring as a direct result of light absorption. The former of these alternatives may be at once dismissed, since apart from all considerations of plausibility the division of the quantum among a number of molecules would provide each molecule with a quantity of energy so small that molecules would receive it frequently from purely thermal sources and consequently a rapid thermal reaction would be anticipated.

Reactions in which a series of processes results from the primary activation of one molecule are not confined to photochemistry and are known as chain reactions, their existence depending upon the faculty possessed by each individual process or link in the chain to prepare the way for the occurrence of the next.

We have already indicated one way in which this can be brought about. In the discussion of the photodecomposition of hydrogen iodide it was pointed out that the occurrence to an appreciable extent of the reaction,



would raise the yield above the observed value of 2 because the hydrogen atom so formed will react according to



Indeed, if (1) were of frequent occurrence an alternation of (1) and (2) would ensue and the yield become very large.

Alternating reactions involving atoms or free chemical radicles provide one type of chain reaction—Atomic Chains, a type which has proved much more common than that first proposed, which we may term Energy or Activated Molecule Chains.

ENERGY CHAINS

According to the activation theory of *thermal* chemical change, reaction only follows from those collisions in which the colliding molecules possess a certain minimum of energy (probably in some particular degrees of

freedom)—the energy of activation. Now the heat of reaction, Q , is the difference between the total energy contents of all the reactants and that of all the resultants (AC in Fig. 5). Before reaction, however, the reactants must have the energy contained in some particular degree or degrees of freedom raised to the value $E/\text{gm. mol.}$ represented by B. Immediately after reaction the resultants will still contain distributed among them the same amount of energy as was contained in the reactants, but this will be greater than their normal

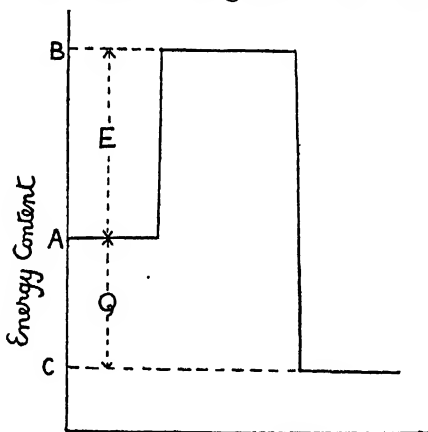
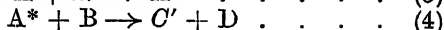


FIG. 5

energy content C (Fig. 5) by the amount BC, approximately equalling $(Q + E)$.

The distribution of the excess energy $(Q + E)$ may be such as to leave it all in the possession of one of the resultants, or it may be divided more or less equally among them, but in either case a sufficiently large value of Q will ensure that one of the resultant molecules contains an excess energy greater than E .

If we now consider a photochemical reaction, in which the absorbed quantum supplies the activation energy, such as



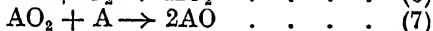
where A^* represents the photo-activated molecule of A and C' , the energy rich resultant containing most of the energy ($h\nu + Q$). If C' now collides with molecule of A before its excess energy has been too far dissipated by intervening collisions, the process



may occur, in which A' is an activated molecule of A not necessarily containing the same quantity of energy nor even containing it in the same degrees of freedom, but nevertheless one which can, when opportunity arises, react according to (4) to produce a new energy rich C' . Processes (4) and (5) can then alternate until the energy of either C' or A' is dissipated, or by some other mischance the chain is brought to an end.

Chain mechanisms of this type were at one time freely postulated, but at the present time their application to reactions with high quantum yields is practically confined to the autoxidations.

A number of substances, in particular aldehydes, can be oxidized in the liquid and gaseous phase by gaseous or dissolved oxygen in the free state (autooxidation). It is supposed that these reactions take place in two stages:



A being the oxidizable molecule and AO_2 an intermediate peroxide which has been in some cases isolated, or had its existence clearly shown, e.g. benzoperacid from benzaldehyde, while acetaldehyde gives a nearly quantitative yield of peracetic acid.

These reactions occur as a result both of thermal and photo-activation of the original molecule A , a chain mechanism being necessitated by the high quantum yields of the photo-processes which range from 10^3 for acetaldehyde to 5×10^4 for sodium sulphite. The chains are supposedly due to the activation of

fresh molecules of A by the transfer to them of the excess energy of the resultants of one of the reactions (6) and (7). When the thermal effect of these processes can be estimated the C' molecule of (4) and (5) can be identified with the products of either (6) or (7). (6) is the more probable when A = benzaldehyde and apparently (7) when A = sodium sulphite. The auto-oxidations are very prone to inhibition by traces of impurities, such as alcohols, this being ascribed to deactivation of the energy rich resultants or—since many inhibitors are themselves substances readily oxidized—to their oxidation by the peroxide, both of which alternatives would shorten the chains and reduce the yield.

The difficulties to be overcome by this sort of chain explain their limited range of application. Activated molecules are not normally found to be capable of retaining their energy undiminished throughout a large number of collisions, but to account for these reactions on the basis of the above hypothesis it is necessary to assume that the activation energy remains but little degraded even after the large number of collisions which the activated molecule must often undergo between its activation according to (5) and collision with a molecule of oxygen, while if the reaction occurs in solution there must also be assumed a similar stability of the energy-rich resultant to collisions with solvent molecules.

The fact that most of the reactions to which the mechanism is applied involve rather heavy molecules invites comparison with the stability of the excited molecules of a fluorescent dyestuff to collision with the solvent, though the quenching of their fluorescence when their own concentrations are raised, renders the comparison less satisfactory. The absorption spectrum also shows in some cases that photo-dissociation of the autoxidizable substance does not occur at the temperatures and wave-lengths used.

It is further essential that one of the stages in the

process should be highly exothermic and this considerably limits the number of reactions to which the energy chain may be applied.

Notwithstanding these and other objections, it must be admitted that there has been devised no other mechanism which will explain the autoxidations and perhaps herein lies the source of any opposition that the energy chain may receive, namely, that in the present state of our knowledge of the stability of energy rich molecules, the mode of transference of this energy from one molecule to another, etc., no proposed mechanism involving activated molecules can either be properly supported or yet definitely opposed by evidence from other sources.

ATOMIC CHAINS

In contrast with the rather unsatisfactory state of the theory underlying energy chains, the investigation of the mechanisms of atomic chains has proved one of the most fertile areas in the field of photochemistry.

Before a discussion of the kinetics of atomic chain reactions can be undertaken, the factors controlling the velocity of reactions in which an atom forms one of the reactants must be considered.

The existing evidence shows that when atoms take part in any *exothermic* process in which two or more resultant molecules are produced, no preliminary thermal activation will be required, that is to say, every collision between the reactants will be effective provided that no steric effects are present. An indication of the way in which such steric effects may operate can be obtained from a consideration of the reaction, $\text{H} + \text{HBr} \rightarrow \text{H}_2 + \text{Br}$. A collision in which the two H atoms come in contact as in (a) Fig. 6, might lead to the desired reaction, whereas a collision such as (b) could not. In practice other and less obvious causes also intervene.

Extending this generalization to *endothermic* atomic reactions, we assume that a preliminary thermal activa-

tion equalling the heat absorbed per mole in the process will be needed before reaction can occur. The number of atoms which react will thus be given by sx for exothermic, and by $sx.e^{-\frac{Q}{RT}}$ for endothermic reactions, where s is a number $<$ unity taking account of the steric factor, and x the total number of collisions between the reactants, and Q the heat absorbed in the endothermic process.

When, however, the atomic reaction is one in which only one resultant molecule is formed, but few of the collisions result in combination even when the reaction is exothermic, and indeed it is this very fact which is the cause of the inefficiency. This will be seen if we

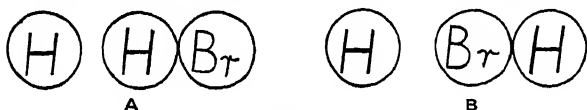
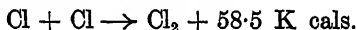


FIG. 6

consider the combination of, say, two chlorine atoms to form a molecule of chlorine.



At the moment of its formation the whole of the heat of combination will be carried by the chlorine molecule, mainly as vibrational energy; but a chlorine molecule containing this amount of energy (now available as the heat of dissociation) will at once or within a time approximating to the period of vibration dissociate again into two chlorine atoms. Unless, therefore, the newly-formed quasi-molecule can get rid of its excess energy within a very short period of time and so become a stable molecule its continued existence is impossible.

It might be thought that the energy would be radiated as fluorescence, but, at any rate as far as the halogens are concerned, conditions favourable for the occurrence of this process only arise with extreme rarity. There is, however, a way whereby the energy can be removed; for should the quasi-molecule collide during its life

with some other body, part at least of the energy can be transferred to it and the chlorine molecule gain stability. Owing to the very short life of the quasi-molecule, what is practically a triple collision or '*dreierstoss*' between the two chlorine atoms and another molecule will be required if permanent combination of the atoms is to occur.

The unsaturated character of atoms also results in their very strong adsorption upon any surface which they strike, i.e. practically every atom coming in contact with a surface remains there. This leads to a further method whereby their combination may be accelerated—a collision between an atom with one already adsorbed upon a surface, which now plays the rôle of energy scavenger. The rate at which an atomic concentration decreases will accordingly be a function of the shape and volume of the containing vessel, and of the total gas pressure, and as might be anticipated from the function of the third molecule in the triple collisions—deactivators—the rate will also depend upon the nature of the molecules present.

Although the detailed analysis of the mechanism of most of the reactions known to involve atomic chains is far from being complete, the problems of the combination of hydrogen with bromine, which in spite of its normally rather low quantum yield exhibits the characteristics of a chain reaction, have been attacked with such thoroughness that the explanation now accepted is unlikely to be much changed by future investigations.

Excepting at low pressures the data for the rate of formation of hydrogen bromide are well expressed by

$$+ \frac{d[\text{HBr}]}{dt} = \frac{K[\text{H}_2] \sqrt{\frac{I_{\text{abs.}}}{p}}}{1 + k \frac{[\text{HBr}]}{[\text{Br}_2]}}$$

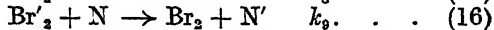
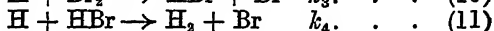
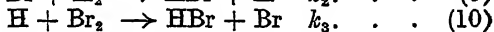
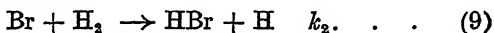
in which $I_{\text{abs.}}$ is the energy absorbed per unit volume per unit time; K and k are constants and p the total

pressure of the mixture of hydrogen and bromine. A similar relation, excepting that $[\text{Br}_2]$ replaces $I_{\text{abs.}}$, is followed by the thermal decomposition. The occurrence of the $\sqrt{[\text{Br}_2]}$ term remained for many years without explanation; such terms, however, follow quite naturally under certain conditions when the reaction originates in a thermal or photo-dissociation.

In the photo-combination of hydrogen and bromine the only substance absorbing light of any of the frequencies which have been used is bromine, and this will certainly be dissociated into its atoms by light of wave-length less than about $510\text{ m}\mu$.



following which the atoms and the products of their reactions might react according to one or more of the secondary reactions.



in which k_1, k_2 , etc., are the velocity constants of the various processes, Br'_2 the quasi-molecule of bromine, and N is any molecule which can carry away the excess energy of the Br'_2 .

In the discussion of the hydrogen iodide decomposition, where a similar series of possible reactions was obtained, it was found that most of the reactions could be disregarded owing to the operation of two principles. Applying similar reasoning here, we find that with the single exception of (9) all are exothermic. Now since hydrogen bromide is only formed in reactions (9), (10) and (12) and the occurrence of (10) and (12) depends upon the formation of atomic hydrogen by (9), it follows that regardless of its endothermic character

(9) cannot be ignored. It will, however, compared with the other—exothermic—processes, in particular (10) and (11) be very slow. The atomic hydrogen will therefore be removed by these two reactions almost as fast as it is formed, and consequently its concentration will be very low. Reaction (13) in which this concentration occurs raised to the second power can therefore be neglected compared with (10) and (11), as can also (12), since $[\text{Br}_2]$ and after an appreciable time also $[\text{HBr}]$ will be $\gg [\text{H}]$.

Remembering that substances whose concentrations are very small will almost instantly reach a stationary concentration when the rate of their formation equals the rate of their removal, i.e. the resultant rate of formation is zero, we obtain the three equations:

$$\frac{d[\text{H}]}{dt} = 0 = k_2[\text{H}_2][\text{Br}] - k_4[\text{H}][\text{HBr}] - k_3[\text{H}][\text{Br}_2] \quad (17)$$

$$\frac{d[\text{Br}'_2]}{dt} = 0 = k_7[\text{Br}]^2 - k_8[\text{Br}'_2] - k_9[\text{Br}'_2][\text{N}] \quad (18)$$

$$\begin{aligned} \frac{d[\text{Br}]}{dt} = 0 = & k_1 I_{\text{abs.}} + k_4[\text{H}][\text{HBr}] + k_8[\text{Br}'_2] \\ & + k_3[\text{H}][\text{Br}_2] - k_2[\text{Br}][\text{H}_2] - k_7[\text{Br}]^2 \quad (19) \end{aligned}$$

Eliminating $[\text{Br}'_2]$ from these and solving for $[\text{H}]$ and $[\text{Br}]$ we find that

$$[\text{Br}] = \sqrt{\frac{I_{\text{abs.}} k_1}{k_7} \left(1 + \frac{k_8}{k_9[\text{N}]} \right)} \quad (20)$$

$$\text{and } [\text{H}] = \frac{k_2[\text{H}_2]}{k_4[\text{HBr}] + k_3[\text{Br}_2]} \sqrt{\frac{k_1 I_{\text{abs.}}}{k_7} \left(1 + \frac{k_8}{k_9[\text{N}]} \right)} \quad (21)$$

the square root being due to the term $k_7[\text{Br}]^2$ in (18) and (19).

The rate of formation of hydrogen bromide is given by (9) + (10) - (11).

$$\therefore \frac{d[\text{HBr}]}{dt} = k_2[\text{H}_2][\text{Br}] + k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}]$$

which agrees with the experimental relation when it is remembered that N is proportional to p if the substances present have all the same deactivating power or their relative concentrations remain unchanged. In the presence of varying amounts of substances having different deactivating powers the denominator of the expression under the root becomes somewhat more complicated.

Before considering the differences in the reaction mechanism which appear at low pressures a few of the points of interest arising out of the higher pressure reaction will be dealt with.

(1) A square root relation between light intensity and rate of reaction is to be generally anticipated when the rate of inception of the chains is proportional to the intensity of the light and the rate of their termination proportional to the square of the number in progress at any moment, or what amounts to the same thing, the square of the concentration of one of the intermediate reactant-resultants of the links of the chain which we may call the catalyst. More generally expressed, if we assume a catalyst to be formed by the light, then the velocity of reaction will be proportional to the square root of the intensity if

- (a) the rate of formation of the catalyst \propto the intensity,
- (b) the rate of the measured reaction \propto the catalyst's concentration, and
- (c) the rate of removal of the catalyst \propto the square of its concentration.

In the present reaction bromine atoms may be taken as the catalysts and the validity of the conditions can be seen from (8), (22), (17) and (19). It might be pointed out that if the chains were ended by either of the reactions (12) or (13) instead of by (14), much more involved expressions would be obtained and the relation between intensity and velocity would depend upon the conditions, becoming linear or square root only as limiting cases.

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pendent of temperature and has a value of about 10 instead of approximately unity as would be the case were every collision between H and Br₂ or H and HBr followed by reaction. The discrepancy is probably to be ascribed to the greater prominence of the steric factor in collisions in which HBr is concerned.

(5) At ordinary temperatures reaction between hydrogen and bromine (both in the light and in the dark) is very slow, and to gain a convenient rate the temperature must be raised to about 170° or so for the photoreaction and rather higher for the thermal. Both reactions thus have a temperature coefficient, that of the photochemical corresponding to an energy of activation of 17,600 calories. We have already seen that the reaction, $\text{Br} + \text{H}_2 \rightarrow \text{HBr} + \text{H}$, is endothermic and it will therefore need a preliminary activation equalling the heat absorbed before it can occur. The heat of reaction can be calculated from the known heats of dissociation of hydrogen and hydrobromic acid, the figure 16,000 calories being obtained. It is exceedingly improbable that any thermal activation will be necessary for the completion of the photodissociation, at any rate with wave-lengths less than $510m\mu$, while the assumption of a temperature coefficient for any of the other secondary reactions at once leads to difficulties. A temperature coefficient for reaction (11) for example, would, on account of the independence of temperature of the ratio $\frac{k_3}{k_4}$, lead to the improbable

conclusion that (12) has a temperature coefficient exactly equal to that of (11). It would consequently appear that the heat of activation deduced from the temperature coefficient and the calculated heat effect of reaction (9) should in fact be identical and the difference—1,600 calories—be due to experimental error.

The thermal combination follows precisely the same mechanism excepting that the bromine atoms now arise from the thermal dissociation of bromine molecules, and the temperature coefficient has to take

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account, not only of the heat of activation of reaction (9), but also of the changing degree of dissociation with temperature, the resultant coefficient being the product of that due to these factors individually.

Low-pressure Reaction. As the total pressure is reduced below a certain limit depending upon the dimensions of the reaction vessel, the relation between intensity and velocity of hydrogen bromide formation begins to change, and with a sufficient reduction in the pressure becomes finally a direct linear proportionality; the smaller the vessel the higher is the pressure at which the transition commences. The explanation lies in the strong adsorption of the bromine atoms by the walls of the vessel.

At the higher pressures the distance which the atom travels between two collisions is small and consequently the number of collisions it will undergo (and therefore its chance of reacting) before reaching the wall will be great. The greater the average distance of the atoms from the walls the greater will be their chance at a given pressure of reacting before reaching the walls. Of course those atoms formed very close to the front wall of the vessel will have at all pressures a very high chance of being adsorbed in preference to being removed by (14) and (16), but the proportion of the total number formed to which this applies will normally be small. At lower pressures the mean free path between collisions will be increased and the concentration of bromine atoms and the chance of a *dreierstoss* much reduced, so that conditions will become favourable for the atoms to reach a surface without meeting another of their kind with which they can combine, and with sufficiently low pressures the chance of such a meeting occurring will be so remote as to be negligible.

The atoms will then be removed at a rate proportional to their concentration (i.e. by diffusion) and the square root relation between intensity and velocity will be replaced by a linear one. The observed velocity-pressure curve at very low pressures can, in fact, be

accounted for by a not improbable value of the diffusion coefficient of bromine atoms.

Thus while the relation, $\text{rate} \propto I^{\frac{1}{2}}$, is usually to be explained by the optical dissociation of some molecular species (other causes may operate on occasion), the absence of such a relation by no means proscribes the occurrence of an atomic chain.

A gaseous reaction showing many points of similarity to the above is the photochemical formation of phosgene from carbon monoxide and chlorine, in light absorbed by the latter, while the combination of hydrogen and chlorine which might be expected to follow a rather similar course, shows actually very different characteristics, and notwithstanding the great quantity of work which has been expended in attempting to unravel its mechanism the difficulties to be surmounted have so far prevented the attainment of more than very partial success. The quantum yield is here very high because the reaction corresponding to (9), $\text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \frac{1}{2} \text{H}_2$, is rapid. The velocity is also proportional to the intensity owing to the removal of the chlorine atoms by a process other than their combination, probably mainly by their combination with molecular oxygen, traces of which are difficult to remove.

In solution a number of reactions having high quantum yields are known and many of them obey the relation, $\text{rate} \propto I^{\frac{1}{2}}$. Among these may be mentioned photo-brominations of unsaturated organic substances, some bromine photo-sensitized reactions, and photo-oxidations by bromine and iodine, the halogen being in all cases the light-absorbing substance. The decomposition of hydrogen peroxide and the autoxidations also appear to follow the same relation under certain circumstances. Some of the above also tend to a linear relation under limiting conditions or have superimposed upon the $I^{\frac{1}{2}}$, a linear relation, a complication less easily explained with reactions in solution than with gaseous reactions.

The uncertainty as to the state of aggregation, col-

the facts, if we further assume the solvent to exert only a secondary influence upon the heat of dissociation.

Since the reaction is inversely proportional to the potassium iodide concentration, i.e. inhibited by this substance, the progressive increase in its concentration during the reaction would unnecessarily complicate the study of the mechanism unless, as is usually done, sufficient is added at the start to enable the iodide concentration to be considered constant throughout the course of the investigation.

The iodide ion and iodine, however, combine together to form the tri-iodide ion (I'_3), and this being an exothermic process, it might be anticipated that the photo-dissociation of the I'_3 into atoms would be of less frequent occurrence than the photo-dissociation of the simple I_2 molecule.¹

Indeed, although the complex ion absorbs throughout the spectral range employed, to account for the observations it must be assumed that only light absorbed by free iodine actually leads to dissociation and reaction.

Taking the equilibrium constant for tri-iodide formation as $K = \frac{[I_2][I']}{[I'_3]}$ we have

$$[I_2] = \frac{K[I'_3]}{[I']} \quad . \quad . \quad . \quad . \quad . \quad (26)$$

Now if α_1 and α_2 are the extinction coefficients of I_2 and I'_3 respectively for the wave-length concerned, the fraction of the total absorbed energy captured by

iodine is $\frac{\alpha_1[I_2]}{\alpha_1[I_2] + \alpha_2[I'_3]}$ which on substitution of the

value of I_2 from (26) becomes $\frac{\alpha_1 K}{\alpha_1 K + \alpha_2 [I']}$. Under the usual experimental conditions (large excess of KI),

¹ Since the light energy has now not only to separate the two atoms from one another, but also from the iodide ion. In addition to this the combination between the molecule and the ion may so change the linkage between the two atoms as to make optical dissociation resulting in an iodine atom impossible.

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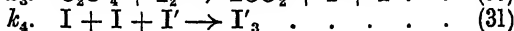
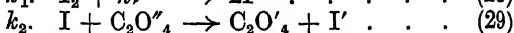
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$\alpha_2[I'] \gg \alpha_1 K$ and consequently the fraction of the light absorbed by free iodine becomes :

$$\frac{\alpha_1 K}{\alpha_2 [I']} \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

The secondary reactions proposed to account for the experimental relation (25) are



Leaving for a moment certain weaknesses in this scheme, the equations for the stationary concentrations of the intermediate substances I and $C_2O'_4$ are :

$$\frac{d[C_2O'_4]}{dt} = 0 = k_2[I][C_2O''_4] - k_3[C_2O'_4][I_2] \quad . \quad . \quad (32)$$

$$\frac{d[I]}{dt} = 0 = \frac{k_2[I_2]I_0}{I'} \frac{\alpha_1 K}{\alpha_2} + k_3[C_2O'_4]I_2 - k_2[I][C_2O''_4] - k_4[I]^2[I']$$

$$\text{whence } [I] = \sqrt{\frac{k_1 \alpha_1 K}{\alpha_2 k_4} \cdot \frac{I_0^2 [I_2]^2}{[I']}} \quad . \quad . \quad . \quad . \quad (33)$$

According to (24) the rate of disappearance of iodine equals the rate of formation of $2CO_2$, i.e. the rate of (30) which from (32) must equal the rate of (29)

$$\therefore - \frac{d[I_2]}{dt} = k_2[I][C_2O''_4]$$

which from (33)

$$= \frac{k_2 k_1 \alpha_1 K}{\alpha_2 k_4} I_0^2 [I_2]^2 [I']^{-1} [C_2O''_4] \quad . \quad . \quad (34)$$

If its concentration is not too high the potassium iodide can be considered as completely dissociated and the term $[I']$ replaced by $[KI]$, thus bringing the theoretical expression into agreement with that found experimentally for the reaction in weakly absorbed light. To understand why the kinetics of the reaction should depend upon the degree of light absorption it

must be realized that when absorption is weak the density of the absorbed energy is practically constant throughout the solution and that the increase in the absorption caused by an increased concentration of the absorbing substance (iodine) is distributed evenly throughout the solution. When absorption is strong, however, apart from the gradient in the density of the absorbed energy in the solution which may be of importance in another connexion, the absorption is confined to a limited volume of the solution, and this volume is decreased by an increase of iodine concentration. If we assume absorption to be complete when the light has been reduced in intensity to $\frac{1}{x}$ of the value

incident on the front surface of the solution $\log \frac{I_0}{I}$
 $= \log x = ahc$, whence if $\log x$ is constant h , the thickness of solution giving this reduction in intensity

$$\propto \frac{1}{(\text{concentration of iodine})}$$

Assuming that the absorption is complete in a volume $V, (\propto h)$ with an iodine concentration C and that the mean velocity $= a$ the total quantity of iodine used will be Va . If now C is increased to nC the volume in which the absorption occurs will become $\frac{V}{n}$, and from

(32) the velocity $a\sqrt{n}$, and therefore the total iodine used $= \frac{V}{n} \cdot a\sqrt{n} = \frac{Va}{\sqrt{n}}$. It is this quantity which is

actually determined and therefore when absorption is strong the measured rate of reaction should be inversely proportional to \sqrt{n} or to $[I_2]^{\frac{1}{2}}$ as was in fact found for blue light.

Perhaps the weakest point in the mechanism lies in reaction (31). The assumption of the simpler reaction $I + I \rightarrow I_2$, leads to the appearance of the iodine concentration in the expression for the rate of reaction

raised to the power $-\frac{1}{2}$ instead of the experimentally found -1 , so that while there is some justification for the assumption of a triple collision between two iodine atoms and an iodide ion, its significance is rather difficult to explain. The function of the ion can hardly be that of excess energy 'scavenger', since in the first place the much greater frequency of triple collisions involving water molecules should suffice to counteract the possibly higher efficiency of the iodide ion for this purpose, while further, since only a single molecule results from the process (31) it is rather to be anticipated that this combination would take place but rarely without the assistance of yet a fourth molecule. The reaction between bromine and potassium oxalate, is stoichiometrically similar but apparently differs in its mechanism since potassium bromide has only a secondary influence upon the rate of reaction. It is therefore to be concluded that the ion Br'_3 is dissociable by light to give bromine atoms and that the process analogous to (31) is replaced by the simpler $\text{Br} + \text{Br} \rightarrow \text{Br}_2$.

A second difficulty arises from a comparison of this reaction with others in which iodine acts as an oxidizing agent, and in which a quite different mechanism is employed to account for the observations. In the reaction between potassium nitrite and iodine for example a reaction between iodine atoms and water to form hypiodous acid is postulated. Neither mechanism for these reactions of iodine in aqueous solution appears quite satisfactory and it is not improbable that the future will see a complete revision of the theory of these and other reactions of aqueous halogens.

Before leaving chain reactions a little must be said concerning the possible interaction of simultaneously occurring photo- and thermal-reactions.

Where a photochemical reaction can only be examined under such conditions that thermal reaction between the reactants is appreciable it can often be assumed that these occur independently of one another and the

amount of photochemical change can then be determined by subtraction of that due to the thermal reaction from the total change observed. Such procedure is not, however, always justifiable, especially with catalytic chain reactions in which the thermal and photo-mechanisms are identical and the velocity of the light process is proportional to the square root of the intensity, i.e. when the light serves merely to increase the concentration of the 'catalyst' above the normal dark value. This can easily be shown.

If the thermal and photo rates of formation of the catalyst are respectively T and P and the rate of destruction of the catalyst, C , is proportional to the square of its concentration, or $-\frac{dC}{dt} = k[C]^2$ we have in the dark; $[C_{\text{dark}}] = \sqrt{\frac{T}{k}}$.

Assuming for the moment that the dark reaction can be ignored, the catalyst concentration in the light will be:

$$[C_{\text{light}}] = \sqrt{\frac{P}{k}},$$

so that if the dark and light reactions are assumed independent of one another, we have, since the rate of reaction is proportional to the catalyst concentration:

$$\text{rate} \propto (\sqrt{T} + \sqrt{P}),$$

but if the catalyst of the dark reaction is identical with that formed by the light it is obvious that no distinction can be made between catalyst molecules from the different sources. Therefore in the light we have

$$+ \frac{d[C]}{dt} = 0 = T + P - k[C]^2$$

$$\therefore \text{rate} \propto [C] \propto \sqrt{\frac{T+P}{k}}.$$

In such a case as the above, to obtain the true photochemical rate or rather its square, the square of the dark rate must be subtracted from the square of the

total rate. Of the reactions considered here it has been shown that the combination of hydrogen and bromine needs this treatment. When, however, the light is very strongly absorbed so that the light reaction is confined to a small fraction of the total volume of the system direct additivity of the dark and light reactions may be anticipated.

Apart from all questions of convenience it is therefore advisable to work under such conditions (low temperature, etc.) that the thermal reaction may be neglected or at least reduced to as small a value as possible. When it cannot be neglected some theoretically sound method should be employed to test whether interaction occurs.

Rather similar to the interaction of dark and light reactions, are the results obtained by illuminating some reactions with two light beams of differing wave-length, the velocity in the mixed light being *lower* than the sum of the velocities obtained with each beam singly, the connexion being similar to that between the dark and light reactions just considered. In other reactions the velocity in mixed light has been found to be faster than the sum of the velocities in the more nearly monochromatic constituents of the mixed light. These effects of mixed light are, however, very difficult to interpret.

CHAPTER IV

THE DEPENDENCE OF THE QUANTUM YIELD ON TEMPERATURE AND WAVE-LENGTH

WITH the exception of those reactions which obey the Einstein equivalence law exactly, that is to say apart from two or three of the reactions so far studied, it is found that the quantum yield, in addition to being a function of the concentrations of the substances present, usually also varies with the temperature of the system, the wave-length of the light employed,

and frequently with changes in other variables. Matters may be further complicated, as, for example, often with the temperature coefficient, by a dependence upon the wave-length of the incident radiation, of the relation between the yield and the variable.

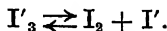
Unfortunately the experimental data are very meagre, and consequently (excepting the methods for determining the mean life of the 'catalyst') any theoretical conclusions which may be drawn or explanations put forward to account for the observations must be considered to be tentative suggestions rather than accepted principles.

As regards the temperature coefficient there is also a risk of confusion owing to the existence of two methods whereby it is determined. Firstly, and this applies in particular to the earlier measurements, there is the temperature coefficient of the amount of chemical change produced in a given time by light of constant *intensity*, and secondly the temperature coefficient of the quantum yield, or the amount of chemical change per unit of *absorbed energy*. These two coefficients will in general only be the same if the energy absorbed in the given time with the same incident intensity is independent of temperature, a state of affairs which exists only if the absorption is total or if the extinction coefficient is independent of temperature. Of these it is the coefficient of the quantum yield which is of importance. Fortunately it is not usual for the extinction coefficient to vary very rapidly with temperature and consequently the velocity temperature coefficient can in many cases be used as a good approximation to the true coefficient, although care is needed if the constancy of the absorption has not been tested. A rough test of the suitability of the velocity coefficient can be made by comparing the coefficients obtained with concentrations giving strong and weak light absorption. If the results are independent of concentration it is unlikely that the extinction coefficient changes appreciably with temperature.

In the following discussion we shall consider only the coefficient of the quantum yield, and although by so doing we shall have removed one source of complication—change of absorption—it is certain that in many cases the temperature coefficient is still the product of coefficients due to two or more processes, the separation of which is a matter of some difficulty. There is normally an inverse relationship between the quantum yield and its temperature coefficient, i.e. the use of shorter wave-length light is accompanied by an increased yield and a decreased temperature effect, possible causes of which will now be considered.

The existence of an internal light filter such as the I'_3 ion in the reaction between potassium oxalate and iodine, due to the combination of the absorbing reactant with the solvent or other substance present to produce an absorbing but non-photo-sensitive compound, leads to a temperature coefficient owing to the changes in the relative concentrations with temperature.

In the discussion of the iodine-oxalate reaction it was shown (page 57) that the fraction of the light absorbed which was usefully employed was $\frac{\alpha_1 K}{\alpha_2 [I']}$ where α_1 and α_2 are the extinction coefficients of I_2 and I'_3 respectively and K the equilibrium constant of the reaction



Now if Q be the heat evolved by the formation of one gm. mol. of tri-iodide ion

$$\frac{d \ln K}{dT} = \frac{Q}{RT^2}$$

and since, if none of the other factors upon which the yield depends are affected by temperature change, $\gamma \propto K$

$$\therefore \frac{d \ln \gamma}{dT} = \frac{d \ln K}{dT} = \frac{Q}{RT^2} \cdot^1$$

¹ The temperature coefficient per one degree

$$= \frac{1}{\gamma} \frac{d\gamma}{dT} = \frac{d \ln \gamma}{dT} = \sqrt[10]{\text{coefficient per } 10^\circ}$$

Thus in the above limiting case the temperature coefficient of the yield is that of the thermal equilibrium constant. If, however, $\alpha_2[I'_3]$ had been of the order of magnitude of $\alpha_1 K_1$, $\frac{d \ln \gamma}{dT}$ would have been less than

$\frac{Q}{RT^2}$ though still of the same sign and in addition the extinction $\left(\log \frac{I_0}{I}\right)$ of the solution would change with temperature and the temperature coefficient cease to be of the Arrhenius type.

The ratio of the extinction coefficient of the reactant to that of the inactive complex will in general depend upon the wave-length, an increase in the ratio causing an increased yield, but only when the product $\alpha_{\text{reactant}} \times [\text{Reactant}]$ is comparable with that of $\alpha_{\text{complex}} \times [\text{Complex}]$ will the temperature coefficient depend on the wave-length and then in a sense opposite to that of the quantum yield.

Temperature coefficients due to solvation may possibly be found to be fairly common since a solvate would normally be expected to have a sensitivity to light differing from that of the simple substance. A reaction in which this effect would appear to operate is the bromine sensitized transformation of the maleic esters into their fumaric isomers, in which complex formation between bromine and the maleic ester has been shown to occur. Of course sufficiently large quanta may be able to dissociate or activate the complex as well as the simple molecule, and then the temperature coefficient will be reduced or eliminated according as whether some or all the complex molecules are made reactive by light absorption.

It might be thought that there would be a sharply defined frequency below which the quanta would not be great enough to produce reaction, either because the energy supplied is insufficient to dissociate the molecule or because it is not sufficiently excited to be

chemically active. Actually the quantum yield is always found to rise over a range of frequencies, as for example occurs in the case of the decomposition of nitrogen dioxide for which the quantum yields at different wave-lengths are shown in Table 2, the alternative values of γ at each wave-length being the results of different observers.

TABLE 2

λ	436	405	365	310-270
γ	0.009; 0.000	0.72; 0.74	1.54; 2.10	2.07

The absence of a sharp threshold frequency is due firstly to the fact that not all molecules absorbing a given frequency have initially the same energy content, secondly, to the possible utilization of the energy of a collision to raise that supplied by the absorbed quantum to a level capable of producing chemical change, and thirdly, to deactivating collisions.

If we consider the case of a non-polar diatomic molecule such as a halogen, whose photochemical activity is due to dissociation, this can only be brought about adiabatically, if the light quantum makes the total energy content of the absorbing molecule up to at least D' —the heat of dissociation of the normal molecule (one in the lowest vibrational level) into a normal and an excited atom.

The observed convergence limit of the band spectrum is usually that of the lowest vibrational level, but if the absorbing molecule was initially in one of the higher vibrational levels, the light energy which must now be absorbed to raise the total energy content of the molecule after absorption up to D' will be lower by an amount equalling the initial vibrational energy, and the minimum frequency producing dissociation correspondingly moved to lower frequencies. There will thus be not one convergence limit with its appended continuum, but several the frequency difference between any two adjacent ones being proportional to the energy difference between the two initial vibra-

tional levels from which they arise. This will perhaps be made clearer by a study of Fig. 7, in which the band systems of a few of the lowest initial vibrational levels are shown diagrammatically.

Frequencies less than that of the highest frequency convergence limit can only dissociate adiabatically those molecules which absorb in a continuum. In the figure light of frequency A , for example, will dissociate only molecules which were initially in the third or higher vibrational levels, the remainder being merely excited. We are in fact dealing here with a rather special case of the internal filter.

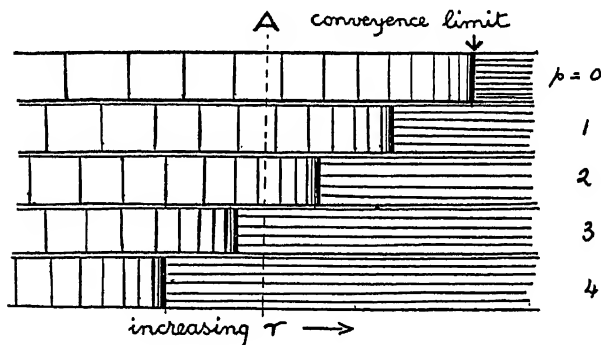


FIG. 7

The fraction of the total number of molecules which are in the n th vibrational level is given approximately by the Boltzman expression, $e^{-\frac{E_n}{RT}}$, E_n being the energy associated with the n th level. The number of molecules in the higher levels is at normal temperatures relatively very small but increases rapidly with rising temperature.

The extinction coefficient for a given frequency radiation depends not only upon this frequency, but also upon the energy content of the absorbing molecule, and for our present purpose molecules in differing levels

may be looked upon as different species in equilibrium with one another. The ratio of the number of absorbed quanta which produce dissociation to the total number absorbed at any frequency is therefore given by

$$\frac{\sum \alpha_c N_c}{\sum \alpha_c N_c + \sum \alpha_D N_D} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (1)$$

in which α_c and α_D represent the extinction coefficient of molecules in levels for which the given frequency lies respectively in a continuous or discontinuous region of their spectrum, and N_c and N_D the corresponding concentrations. In the absence of other factors this expression also gives the ratio of the quantum yield at the frequency to its value at frequencies greater than that of the highest frequency convergence limit.

Although N_c will usually be negligible compared with N_D in regions where band absorption occurs, the dependence of the extinction coefficient upon the vibrational level forbids the assumption that $\sum \alpha_c N_c \ll \sum \alpha_D N_D$. Nevertheless the yield must finally decrease with the frequency.

Since rise of temperature produces an increase of N_c at the expense of N_D , the above expression shows that a temperature coefficient of the yield is to be anticipated in a band region and that this coefficient will increase as the yield decreases.

Reliable data enabling a test of the above expression to be made are non-existent, but it is doubtful whether, excepting for gaseous systems at low pressures, it will be applicable, for there are two factors which militate against it when the conditions are such that the excited molecules may undergo a collision during their existence. First there is the possibility of the energy of the excited molecule being sufficiently augmented by a collision of the first kind to raise the energy up to D' , and secondly, collisions may produce a readjustment of the energy distribution within the molecule in such a way that dissociation may follow if the energy content after absorption exceeds the thermal heat of dissociation. Both these processes would increase the

yield above that given by (1), the second being probably of the greater importance. Suggestive evidence of the occurrence of this second process is to be found in the persistence of a considerable velocity or quantum yield with reactions involving iodine and bromine down to frequencies approximately corresponding to the thermal heat of dissociation.

The suggestions so far considered do not seem capable of accounting for the gradual rise in the quantum yield over a very wide range of frequencies such as occurs in the hydrolysis of the chlorplatinic acids and decomposition of potassium nitrate as shown in Tables 3 and 4.

TABLE 3

Hydrolysis of Tetrachlorplatinic Acid

λ	2378	2482	2655	3100	3660	4350	5460 Å
γ	4.7	2.8	1.5	0.07	0.026	0.0033	0.0009

TABLE 4

Decomposition of Potassium Nitrate

λ	207	253	282	302	313 $m\mu$
γ	0.25	0.17	0.024	0.013	0.010

The figures for the two highest wave-lengths in Table 4 were obtained under rather different conditions to the first three and are therefore only roughly comparable therewith.

Results such as the above are usually explained by the postulation of yet a third collision process—deactivation of an excited molecule before it can react.

The existing experimental work on the deactivation of excited molecules is of very little assistance in the present problem, and the chemist can account for his results by assuming either that the collisions only partially deactivate the excited molecule and that the chance of sufficient energy being left to produce a chemically active molecule is greater, the greater the energy of the absorbed quantum, or that if complete deactivation occurs as a result of a collision that the stability of the excited molecule increases with the size of the absorbed quantum.

sufficiently high frequencies a collision of the first kind between the excited atom and a molecule might produce dissociation of the latter and thereby an increase in the yield.

Concerning the influence of temperature on the deactivation processes considered here, little can be said. There exist rather uncertain indications that the fractional number of collisions between excited and other molecules which result in deactivation, decreases with rising temperature, but another interpretation of the results is possible, and indeed evidence from other sources would suggest that the deactivating efficiency of collisions is independent of temperature.

Under certain circumstances the normal relationship between the yield and wave-length may be reversed and a decreasing yield with decreasing wave-length be obtained. An interesting case in which such an effect has been observed is the decomposition of acetaldehyde when the wave-length of the light is reduced below about $230 m\mu$. The explanation lies in what may be termed an intramolecular light filter.

The molecule $\text{CH}_3-\text{C} \begin{array}{l} \nearrow \text{H} \\ \searrow \text{O} \end{array}$ contains two light-ab-

sorbing electronic systems, or chromophores. Firstly there is an absorption band due to the $>\text{CO}$ group extending either side of a maximum of absorption at about $280 m\mu$, and, secondly, there commences at about $230 m\mu$ a second band whose maximum must lie well below $200 m\mu$.

It is only by activation of the carbonyl group that decomposition can be induced, and consequently only light absorbed in the long wave band is chemically effective. In the region between $220 m\mu$ and $240 m\mu$ the two bands overlap, the absorption being due almost entirely to $>\text{CO}$ at $240 m\mu$ and to $-\text{CH}_3$ at $220 m\mu$.

Reactions involving atoms may show a similar wave-length effect, but for a very different reason. An example is the decomposition of hydrogen iodide in

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hexane solution. The extinction coefficient of the solution increases continuously with decreasing wave-length throughout the range employed, and consequently the concentrations of the hydrogen and iodine atoms formed will be also increased by a decrease in wave-length. This can perhaps be better appreciated if a solution is considered that is so dilute that at all wave-lengths the absorption is slight and with which therefore the energy absorbed will be proportional to the extinction coefficient. Under otherwise identical conditions decrease of wave-length will on account of the increase in α cause more quanta to be absorbed in a given volume of solution and therefore the rate of increase in the atomic concentrations to be raised. Higher concentrations of atomic hydrogen will favour the reaction $H + H \rightarrow H_2$ in which it occurs to the second power to a greater extent than that in which it occurs only to the first power, $H + HI \rightarrow H_2 + I$, with a corresponding reduction in the quantum yield. If this explanation is the true one the rate of reaction should deviate from exact proportionality to the intensity.

For similar reasons the yields of reactions in which the rate of reaction is proportional to the square root of the intensity should show a similar inverse relationship to the extinction coefficient, which (since in most photochemical work only the long wave-length side of an absorption band has been used) will usually mean that the yield will decrease with decreasing wave-length.

For the sake of simplicity still confining attention to conditions such that absorption is weak and making use of the conditions assumed to be the cause of this type of reaction; we have in the steady state of the catalyst concentration

$$\frac{d[\text{Catalyst}]}{dt} = 0 = k_1 I_0 a h c - k_2 [\text{Catalyst}]^2$$

$$\therefore [\text{Catalyst}] = \frac{1}{k_2^{1/2}} \sqrt{k_1 I_0 a h c}$$

in which k_1 and k_2 are the velocity constants for the

processes a and b of page 51, and a , h , c and I_0 have the usual significance. The quantum yield being proportional to the rate of reaction divided by the absorbed energy ($\propto ahcI_0$) the expression (2) leads to

$$\gamma \propto (acI_0)^{-1}$$

an expression which closer analysis shows to be also valid when absorption is total. With this type of reaction, therefore, provided that a is the only factor dependent upon the wave-length, the yield will be an inverse function of a . In this connexion it might be noted that the small difference between the quantum yields of hydrogen bromide formation in passing from blue to green light may be due to partial compensation of changes in the yield due to the decrease in the extinction coefficient, and those due to other effects arising out of the increase in the wave-length. Such an effect of the extinction coefficient has been found qualitatively in the case of the decomposition of hydrogen peroxide and the reaction between potassium oxalate and iodine.

Changes in viscosity or rates of diffusion with temperature can produce quite considerable temperature coefficients if the light is so strongly absorbed that the absorption is practically complete within a very short distance of the front surface of the reaction vessel, thereby causing very large concentration gradients of the intermediates and even of the reactants themselves. Any factors tending to reduce or remove these gradients will in doing so frequently also raise the quantum yield. Elevation of temperature or stirring of the solution are such factors. Stirring, if sufficiently vigorous, by reducing the concentration gradients will reduce temperature coefficients arising in this way, and at the same time raise the quantum yield.

The temperature coefficients of the reaction between iodine and potassium oxalate obtained with light of wave-length $366m\mu$, given in Table 6, show very well the magnitude to which this effect may attain.

TABLE 6 ¹

	No stirring.	Slow stirring.	Rapid stirring.
Temperature coefficient	4.96	3.77	3.10

Temperature coefficients so produced will increase with the extinction coefficient (owing to the greater concentration gradients) and will not, therefore, necessarily follow the usual rule that the use of shorter wave-lengths is accompanied by a reduction in the temperature coefficient.

Liquid phase reactions may be affected by the decrease in viscosity which follows from a rise of temperature (and this applies equally to photo-chemical and thermal changes) producing an increased velocity and quantum yield on account of the enhanced collision rate.

In the last chapter it was shown that the temperature coefficient of hydrogen bromide formation was that of one of the reactions of the chain. This supplies the last of the sources of a temperature coefficient considered here—the coefficient due to the necessity of thermal activation for some essential link or links (other than the initial photo-process) of a chain reaction. This type of temperature coefficient, since it is in no way directly connected with the light absorption, should, of course, be independent of the wave-length of the light employed.

As there is no reason why several of the above factors should not be operative at the same time, it follows that the relations connecting the quantum yield with wave-length and temperature may be highly complicated and their analysis correspondingly difficult. The photochemical temperature coefficient will, however, usually be less than that of the corresponding thermal process, as the thermal activation needed for the primary process (dissociation or formation of an activated molecule) will be lower in the photochemical reaction.

¹ The author is indebted to Professor Allmand for permission to use these as yet unpublished figures obtained by Mr. K. W. Young.

Before closing the discussion of the temperature coefficient mention must be made of certain exceptional features.

What may be termed the normal coefficients give a constant value of E in the Arrhenius expression $\frac{d \ln \gamma}{dT} = \frac{E}{RT^2}$, and most of the sources of a temperature coefficient we have mentioned should conform to this type or give values of E *decreasing* with rising temperature. Of the few reactions which have been examined at a number of temperatures, however, several have temperature coefficients which *increase* with rising temperature; for example the photo-combination of hydrogen and oxygen and carbon monoxide and oxygen and the bromine sensitized maleic fumaric transformation. Up to the present there has been only one definite proposal which will account for this anomalous behaviour, the theoretical basis of which is shortly as follows.

If one of the secondary reactions following the initial photo process is highly exothermic it is possible that occasionally the energy of the products of this secondary reaction may be utilized to activate a molecule of the light absorbing substance for chemical change (or some other molecule so as to produce the same result), and so set in motion a second set of reactions or reaction chain without the absorption of a second quantum. Since, however, not every energy-rich resultant molecule will at once meet with a suitable reactant molecule but will first undergo a number of deactivating collisions we can assume that an average thermal activation Q_2 will be needed before the collision can initiate a new chain. Thus each chain will start

$Be^{-\frac{Q_2}{RT}}$ new chains, B being a constant accounting for the collision number, steric factors, etc., and the total number of chains started per absorbed quantum will under ideal conditions be

$$1 + Be^{-\frac{Q_2}{RT}} + B^2e^{-\frac{2Q_2}{RT}} + \dots \quad (2)$$

The expression for the quantum yield will be made rather more general if we assume the necessity of thermal activation (or some other factor leading to an Arrhenius type temperature coefficient) of the absorbing molecule before the absorbed quantum can start the chemical change. We then have

$$\gamma = AI_0 e^{-\frac{Q_1}{RT}} (1 + Be^{-\frac{Q_2}{RT}} + \dots) = \frac{AI_0 e^{-\frac{Q_1}{RT}}}{\left(1 - Be^{-\frac{Q_2}{RT}}\right)} \quad (3)$$

Differentiation of this expression leads to a temperature coefficient of γ which increases with rising temperature provided that Q_2 is not too small. It will be seen that when $Be^{-\frac{Q_2}{RT}}$ equals unity an infinite yield or explosion is obtained.

The process envisaged here is free from the objections which can be raised against the 'energy chain reactions' discussed in Chapter III, since there has to be assumed neither any special stability of the energy-rich molecule nor the frequent occurrence of the transfer process.

INFLUENCE OF SOLVENT, ETC.

The quantum yield of many reactions, and probably of all, is susceptible to changes in the solvent. For the present purpose the solvent may be considered to be changed if substances other than the reactants are added to the solution, since there will thereby be produced essentially the same effect, viz. a change in the environment of the reacting and absorbing molecules as if the original solvent were entirely replaced by some other.

Where deactivation of excited molecules by the solvent can take place we have already seen that the extent to which deactivation will affect the yield should depend upon the nature of the solvent molecule. The deactivating power of gases often seems to increase with their electro-negativeness, while for liquid solvents

some such property as the polarity of the solvent may be of importance though doubtless the existence of any such connexion will be often masked by other effects.

The solvent can also exert a very considerable influence upon the yield either by solvating the reactants or by changing their stability through the agency of the very powerful electric fields which surround all but the most symmetrical molecules. A considerable body of data referring to absorption spectra of substances in various solvents is available. Normally the greater the polarity (dielectric constant) of the solvent the greater is the difference between the spectrum of the dissolved and that of the gaseous substance. Three main changes may occur, the whole band may be moved bodily in the direction of longer or shorter wave-lengths, the absorption may be altered in intensity or the character of the spectrum may be changed, the first two of these frequently occurring simultaneously.

A shift in an absorption band to longer wave-lengths will indicate a decreased stability of the part of the molecule responsible for the band in question and a shift to shorter wave-lengths an increased stability. Such decreased stability, for example, will suggest that a light quantum of given magnitude will be more readily able to produce a chemically activated or a dissociated molecule and that therefore a higher yield might be expected, or in the case of thermal reactions that the energy of activation will be reduced and consequently the rate of reaction increased. One or two reactions in which there is a close parallelism between the position of the absorption maximum and the thermal rate of reaction have been investigated.

Attempts to correlate the rate of reaction of photochemical and thermal reactions with the dielectric constant of the solvent have so far met with poor success, and it remains to be seen if the recent work upon dipole moments and in the field of spectrophotometry will prove more fruitful.

When the reactants are electrolytes, their degree of ionization or thermodynamic activity will depend upon the nature of the solvent, and the quantum yield be affected on this account. No great success has attended the attempts to connect the rate of thermal chemical change with activity, and an uncertainty as to the connexion between the photochemical rate and the activity must therefore exist.

In all these solvent effects (apart from certain reactions very sensitive to the P_H) the magnitude is of a totally different order to the catalysis or inhibition mentioned in connection with chain reactions, where catalyst concentrations of the order of 10^{-6} may produce considerable velocity changes, whereas changes produced by the addition of electrolytes, etc., to the reacting system are often only appreciable when the concentration of the addition is of the order of one molar.

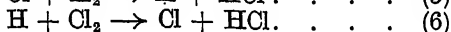
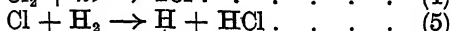
In the discussion of the hydrogen bromide reaction at low pressures it was shown how the surface of the reaction vessel may reduce the length of the chains. It has, however, been found that solid surfaces can also exert a positive catalytic influence. An acceleration of thermal reactions by surfaces owing to the decreased energy of activation needed for adsorbed molecules is common. It does not seem probable that the efficiency of the primary photo-process could be measurably affected in this way and it is more likely that some link of the chain (for surface acceleration has only been observed in chain reactions) is catalyzed by a surface. The photo-decomposition of hydrogen peroxide shows this effect to a marked degree, the rate of reaction being enormously reduced when care is taken to ensure freedom of the solution from dust particles and that the surface of the reaction vessel is as smooth as possible.

As mentioned on page 39 some at least of the secondary processes of the bromine sensitized ozone decomposition apparently take place on the surface of the reaction vessel.

MEAN LIFE OF THE CATALYST AND DURATION OF INDIVIDUAL CHAINS IN CHAIN REACTIONS

The fact that the number of intermolecular collisions which occur in a given period of time is finite, necessitates the existence of an interval of time between the initiation of a reaction chain and its termination. The average of this time interval over all the chains in progress is often spoken of as the 'mean life of the catalyst'.

The use of the term catalyst in this sense may lead to slight confusion, for if we consider the simple Nernst sequence of reactions for the formation of hydrogen chloride



ending by, say, $\text{Cl} + x \rightarrow ? \quad . \quad . \quad . \quad . \quad . \quad (7)$

the average of the intervals between the occurrence of (4) and (7) is to be understood by the mean life of the catalyst. This is not the same as the mean period of existence of the individual chlorine atoms (which might be considered to be the catalyst), nor even this quantity multiplied by the number of links in the chain, nor is there any simple relation between the mean life of the catalyst and these other quantities.

There are available two quantitative methods by which the mean life of the catalyst may under certain circumstances be determined. One is suitable for reactions in which the rate of reaction is proportional to the square root of the intensity and the other to certain gas reactions when a direct proportionality exists.

For reactions with which the square root of intensity relation holds the following equations can be assumed (see page 51),

$$\frac{d[\text{Catalyst}]}{dt} = k_1 I_0 \quad . \quad . \quad . \quad . \quad . \quad (8)$$

$$-\frac{d[\text{Catalyst}]}{dt} = k_2[\text{Catalyst}]^2. \quad . \quad . \quad (9)$$

As a result of these and since the rate of reaction is proportional to [catalyst], the instantaneous rate will not attain its full value immediately upon the commencement of the insolation, nor will the reaction cease as soon as the light is cut off, and it can be easily seen from (8) and (9) that the initial and end effects will not exactly compensate one another, although with sufficiently long periods of illumination the difference will be negligible.

As the duration of the illumination is reduced, however, the lack of compensation will make itself apparent by an increase in the quantum yield owing to the decrease in the average concentration of the catalyst and consequent longer life. In practice use is made of a rotating sector, that is an opaque disk from which one or more sectors have been removed and so rotated in the light beam as to cause the light falling upon the reacting system to be intermittent. (Any other means which gives the same result would serve equally well.) If the sectors removed total 180° (other cases can be dealt with on similar lines), and the rate of rotation is very slow the interposition of the rotating sector in the beam will merely reduce the actual *time* of illumination, and therefore the amount of chemical change, to one-half of that obtained in its absence in the same total time.

On the other hand, with very high uniform rates of rotation, such that the individual periods of illumination are short compared with the mean life of the catalyst, a different reaction rate will be found. During each short period of illumination the catalyst concentration will be increased only very slightly, and similarly the decrease in concentration during the succeeding dark period will be correspondingly small and will after sufficient time has elapsed from the commencement of the insolation be exactly equal to the previous increase. The concentration of the catalyst if plotted

against time will therefore be represented by a slightly sinuous line, rising rapidly at the beginning of the insolation, and later running parallel to the time axis until the light is cut off, whereafter a steady decrease to zero will follow.

The virtual constancy of the velocity and catalyst concentration will justify a treatment similar to that employed for steady illumination. In the present case since the catalyst is only formed during one half of the duration of the reaction (the periods of illumination) the total amount of catalyst formed in unit volume will be $\frac{1}{2}k_1I_0$.(duration of the reaction); which can be rewritten as $k_1\frac{I_0}{2}$.(duration of the reaction). Thus with high rates of rotation the sector behaves as though it had reduced the intensity of illumination to one-half, and therefore the rate of reaction to $\frac{1}{\sqrt{2}}$, of the values obtained without it.

By reducing the rate of rotation of the sector from very high to very low speeds the rate of reaction is changed in the ratio $\frac{1}{\sqrt{2}} : \frac{1}{2}$, or 1 : 0.701.

With a sector as above described the ratio of the velocity obtained with a given rate of rotation to that with an infinite rate is deducible from equations (8) and (9) and is given by the expression : ¹

$$\frac{1 + \ln \frac{Z_1 + 1}{Z_2 + 1}}{\sqrt{2}(Z_1 - Z_2)}$$

in which Z_1 and Z_2 are a pair of numbers which simultaneously satisfy the equations

¹ The author is indebted to Mr. M. J. Pollard of the Mathematical Department, King's College, London, for suggesting this simplification of the original expression. *J.C.S.* (1926), 562. Our $Z = 1/y$.

$$\ln \left\{ \frac{Z_2 + 1}{Z_2 - 1} \cdot \frac{Z_1 - 1}{Z_1 + 1} \right\} = 2(Z_1 + Z_2)$$

and $(Z_1 - Z_2)$ = duration of one light or one dark period \div the mean life of the catalyst.

In the reaction between iodine and potassium oxalate the mean life under various conditions has been found to vary between 0.03 and 0.12 second and in other reactions values of the order of 1 second have been observed.

The second method depends upon the very high rate of adsorption of atoms and free radicals, nearly every such atom or radical which meets with a solid surface remaining there. Reactions in which these highly unsaturated bodies play an essential part in the chain mechanism will, therefore, be reduced in velocity (and quantum yield) should an appreciable fraction of them reach the walls of the vessel. Provided that the vessel is large and the light is not totally absorbed within a short distance of the front surface, this effect will be unnoticeable, but if the conditions are altered so that an appreciable fraction of the chains are initiated at a distance from a surface comparable with that which the atoms or radicals diffuse during the life of the chain the velocity will be reduced.

In the actual experimental determination of the duration of the chains of the hydrogen-chlorine combination, the mixed gases were enclosed in narrow capillary tubes of different bore, and the mean life deduced with the aid of an expression connecting it with rate of reaction in a tube of given bore relative to that in a large vessel. Values between 0.002 and 0.09 seconds were obtained and it was found that among other factors the mean life depended upon the oxygen concentration.

CHAPTER V

EXPERIMENTAL METHODS

THE experimental side of photochemistry may be divided into three sections: (1) the spectroscopic investigation of the light-absorbing substances; (2) the optical system and energy measurements; and (3) the determination of the amount of chemical change. Of these it is only the second which involves a technique specially developed for the subject.

(1) The preceding chapters will have indicated the great value of a study of the absorption spectrum of the absorbing reactant, especially if it can be obtained in the gaseous state, in deciding upon the nature of the initial photo-process. With diatomic molecules, for which no uncertainty as to the products of dissociation can exist, these data are particularly valuable. When the spectrum of the vapour cannot be obtained, the absorption in the liquid or dissolved substance is of use as indicating the regions of the spectrum in which photochemical reaction can be anticipated, while further when the necessary thermal data are available, the possibility of the occurrence of any postulated primary process within the absorption band can be tested.

In addition to this, a point of more direct practical importance arises when internal filters are present or are created during the course of the reaction owing to the formation of a light-absorbing product. Under these circumstances the true quantum yield of the process can only be deduced with the aid of an accurate knowledge of the extinction coefficients of the substances concerned. Again when only a small fraction of the incident radiation is absorbed a more accurate evaluation of the quantum yield can usually be obtained by calculation of the absorbed energy than by attempting to measure small energy differences.

(2) *Light Sources and Isolation of the desired Spectra*

a constant width of spark gap is maintained the variations amount to about 5 per cent. of the mean. Nevertheless, with care the quantum yields obtained with light from a spark do not compare unfavourably with those obtained with other sources. Minor disadvantages are: the necessity for rather high power (2 or 3 kw.) and voltages (10,000 to 20,000 being recommended), compared with the few hundred watts and low voltages which give satisfactory results with other sources, and also their noisiness and the constant attention they require.

Arcs between electrodes of carbon, tungsten and other solids in air, although they have been used, are not entirely satisfactory as sources for quantitative work owing to their unsteadiness and the complexity of their spectra.

The source *par excellence* is the mercury arc in quartz which emits a considerable number of strong conveniently spaced lines, many of which may be isolated by means of filters. Owing to its great importance the quartz mercury arc has been considerably developed, and so many different designs of burners are available that little difficulty should be experienced in obtaining one suitable for any particular set of conditions. The usual vacuum type of arc has its strongest lines in the visible and longer ultra-violet, but if the resonance lines are required their intensities relative to the other lines are very much enhanced if the vapour pressure of the mercury is lowered by strongly cooling the arc tube and reservoirs. This type is almost essential for the investigation of mercury-sensitized processes, owing to the reversal of the resonance lines at the higher pressures. If one of the mercury reservoirs is open to the air so that the arc burns at atmospheric pressure a very intense source is obtained which can be further modified so as to be especially suitable for use with a monochromator by giving the arc tube the form of a capillary of from 2 to 4 millimetres bore.

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The chief lines of the mercury arc are at approximately 579, 546, 436, 405, 366, 313, 303, 265 and $254m\mu$. Similar arcs, in which molten cadmium or alkali metals replace mercury, have also been used and would appear to have great possibilities.

For the isolation of any required spectral region either light filters or a monochromator may be used. When the highest purity of light is desired, especially in the shorter ultra-violet region for which no good filters exist, some form of monochromator, i.e. spectroscopically fitted with a slit at the focus of the telescope lens is essential. Apparatus of quite simple construction is capable of giving very satisfactory results, although unless a specially designed source and large lenses and prisms are used, the energy issuing from the telescope will be low compared with that obtained by means of light filters, rather too low to give a convenient rate of reaction with many processes having small quantum yields. With a continuous source sufficient energy will usually only be obtained if the slits are so wide as to embrace a considerable range of frequencies.

When the use of a monochromator is impossible or inconvenient and the greatest purity is not desired, recourse may be had to light filters. Ideally these are made up of substances having sharply defined limits of transmission, one or more being combined so as to absorb all but the required spectral region or line. It is important that the substances employed should not undergo photochemical or other changes while in use. This condition precludes the use of many of the organic substances which are otherwise suitable, and colloids and other substances whose transmissions are often highly susceptible to changes in the hydrogen ion concentration.

The safest filters are to be found in solutions of inorganic salts and in the numerous coloured glasses on the market. Good filters are available for the mercury lines at 546, 436, 405 and $366m\mu$. If visible radiation is inactive pure potassium chromate has a

sharp transmission band in the $313m\mu$ region, but absorbs all the rest of the ultra-violet down to $254m\mu$. With this filter the blue and violet lines may be removed by either nitrosodimethylaniline or gaseous bromine, in certain cases it would also be advisable to remove the small amount of radiation below $254m\mu$ which these combinations transmit. Gaseous chlorine and bromine if prevented from mixing may be used together to isolate the region below $270m\mu$ when the green and yellow lines are inactive. To remove the infra red, water, or better a strong solution of ferrous sulphate, may be used, the latter, however, absorbs the ultra-violet and can only be used for the visible.

For many purposes strict monochromatism is inessential and the absorbed energy will be restricted to a sufficiently narrow range of frequencies by the experimental arrangements. With reactions in which bromine is the absorbent and when a filament lamp is the source, the absorbed energy is almost entirely confined to the blue and violet region of the spectrum.

The variation of the incident intensity may be procured in a variety of ways. Wire gauze screens, a rapidly rotating sector of variable aperture (cf. page 80), a neutral wedge, a pair of Nicol prisms, variation of the distance between the source and the reaction vessel, and in the running conditions of the source and even of the number of sources have all been successfully employed. Gauzes, rotating sectors and possibly neutral wedges of cathodically deposited platinum, do not alter the spectral distribution of the energy they transmit and may therefore be used with complex light, or when once their transmissions have been determined for one wave-length, may be used for others without the necessity for further energy measurements. With the other methods the direct measurement of each intensity is advisable.

For the measurement of the incident or absorbed radiant energies, bolometers, thermopiles or photo-electric cells may be employed. When absolute energy m^c

The type of bolometer usually employed consists of thin platinum strip forming one arm of a Wheatstone bridge, the change of resistance when warmed by the incident radiation being measured.

In the actual measurements of the absorbed energy the losses due to reflection at the front and back surfaces of the vessel and possible absorption by the walls or solvent must be estimated and corrected for. This is best accomplished by (1) measuring the energy transmitted by the vessel when full of pure solvent, or if the reaction is a gaseous one, when evacuated or filled with a non-absorbing gas, and (2) by then filling the vessel with the reactants and again measuring the energy transmitted. The difference between (1) and (2) gives the energy absorbed. The intensity actually incident upon the front surface of the reactants will be that measured without the interposition of the reaction vessel less that reflected and absorbed by the front wall. When the solvent is perfectly transparent the incident intensity will be the mean of the intensities in front of and behind, the reaction vessel containing solvent only.

If desired the reflection losses may be calculated from the formula

$$\text{Fraction of incident energy reflected} = \left(\frac{n_1 - n_2}{n_1 + n_2} \right)^2$$

where n_1 and n_2 are the refractive indices of the substances on either side of the surface. For a quartz-air surface these losses amount to between 4.5 and 5.5 per cent. and increase with the frequency; the losses at liquid-glass and liquid-quartz surfaces can for most solvents used in photochemical work be neglected, as may also the light reflected back into the system from the back surface of the vessel, if the light is strongly absorbed. When the absorption is weak, however, this correction must be taken into account, as the absorption will be increased by about 5 per cent.

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When only a very small fraction of the incident energy is absorbed, whether owing to the small extinct⁺

of the absorbing system or because a light filter transmitting much inactive radiation is employed, it is often more accurate to calculate the absorbed energy.

In the second case a knowledge of the relative energies transmitted by the filter at different wave-lengths will be required.

The type of reaction vessel to be employed will depend upon the nature of the reaction, the region of the spectrum to be used, the method whereby the progress of the reaction is to be followed and whether energy measurements are to be made. When the only consideration is the disentanglement of the reaction mechanism, the highest possible rate of change is desirable in order to save time and reduce possible complications from a thermal reaction. For this purpose any shape of vessel may be employed, and a frequently used arrangement is shown in cross-section in Fig. 8A. Here A is the source, B an annular vessel containing water to remove heat radiation, and C the annular reaction vessel. If a light filter is required it may either be dissolved in B or placed between B and C. For many purposes such efficient utilization of the energy will not be necessary and flasks or cylindrical vessels placed at a convenient distance from the source may be employed. When the rate of reaction is measured by the rate of decrease of the concentration of one of the reactants the thickness of the vessel should be such that absorption does not exceed 30 to 50 per cent. of the incident energy, since the rate of decrease in the concentrations is greatest when absorption is weak. Other reasons for using weak absorption when determining the mechanism have been mentioned earlier.

When accurate measurements of the quantum yield are to be made it is almost essential that the reaction vessel should possess two plane surfaces parallel to one another through which the light beam may enter and leave the system without distortion. A common type of vessel is shown in Fig. 8B. The material of

which the vessel is constructed, especially those parts through which the light passes, will depend upon the wave-length to be used. Glass is practicable down to the mercury line at $366m\mu$, and special glasses to about $300m\mu$. Below these limits crystal quartz or good fused silica may be used down to the region in which absorption by oxygen becomes important. For the very short wave-lengths ($\lambda < 180m\mu$) fluorite is necessary. Poor quality fused silica may show a detectable absorption in the violet and very considerable absorption below $300m\mu$. In cells of the type

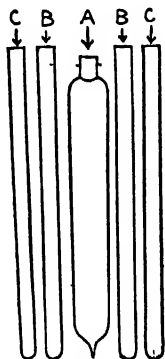


FIG. 8A

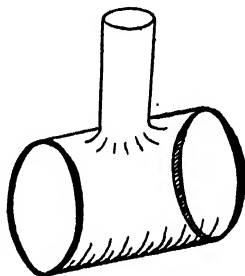


FIG. 8B

shown in Fig. 8B the end-plates may be either fused on to the body if this is of the same material or stuck on with a cement.

Although many photochemical reactions have temperature coefficients so low that no special precautions against temperature changes are necessary to obtain reproducible results, in others thermostating is essential, this being especially so when there is an appreciable dark reaction.

(3) The measurement of the amount of chemical reaction may be carried out in so many ways that no attempt can be made to do more than indicate a few

which stands in a close relationship to two other rapidly advancing branches of knowledge—chemical kinetics and atomic physics.

Apart from the discovery and development of new methods and types of reaction, there is still much to be done along the present lines of advance. An increase in the knowledge of the general properties of chain reactions and their 'catalysts' and the individual idiosyncrasies of particular chains is desirable, while few if any even of the simpler reactions have been so thoroughly studied that nothing further is to be gained by their fuller investigation.

Many of the simpler reactions afford opportunities for the study of the chemical properties of excited or activated molecules under relatively simple chemical conditions. The knowledge so gained will require confirmation and extension from other sources, and the physicist can place himself still further in the debt of the photochemist by throwing more light on the conditions under which such molecules are formed and can exist, and the factors concerned in deactivation processes.

In the limited space at his disposal the author has attempted to give a fair outline of the present state of photochemistry without going too far into details or tracing the development from their progenitors of the theories at present in favour. It must be admitted that this is liable to suggest a stability which may, in fact, be non-existent, and there is appended therefore the following bibliography which contains the chief text-books in English, and references to the periodical literature for the more important subjects discussed.

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